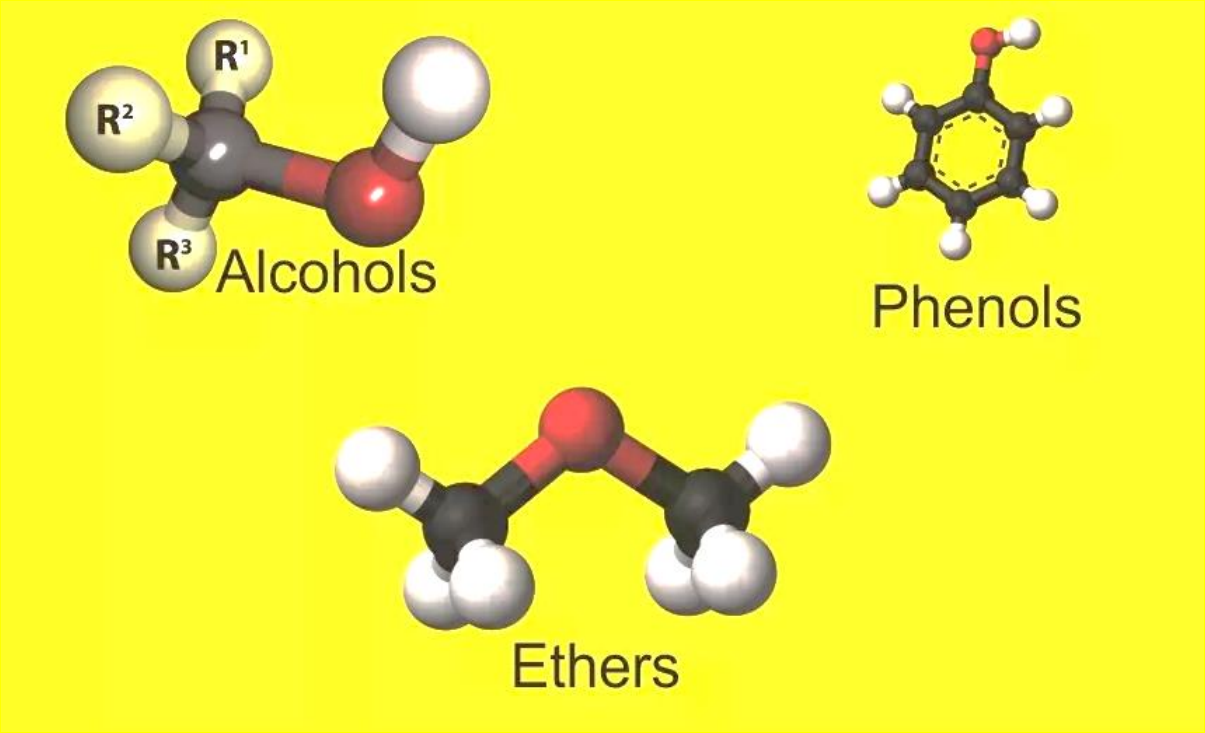
11. Alcohols, Phenols and Ethers



Chemistry Smart Booklet

Theory + NCERT MCQs + Topic Wise Practice MCQs + NEET PYQs

ALCOHOL, PHENOL AND ETHER

ALCOHOLS

METHODS OF PREPARATION OF ALCOHOLS

From alkenes, by acid Catalysed Hydration:

$$>C=C< + H_2O \xrightleftharpoons{H^+} >C(H)-C(OH)<$$

eg. $CH_3-CH=CH_2 + H_2O \xrightleftharpoons{H^+} CH_3-CH(OH)-CH_3$

FROM HYDROBORATION OXIDATION

$$CH_3-CH=CH_2 \xrightarrow{(H-BH_2)_2} CH_3-CH(BH_2)-CH_2$$

$$(CH_3-CH_2-CH_2)_3B \xleftarrow{CH_3-CH=CH_2} (CH_3-CH_2-CH_2)_2BH$$

$$3CH_3-CH_2-CH_2-OH + B(OH)_3$$

Propan-1-ol

Reduction of Aldehyde, Ketone and Carboxylic Acid

$$R-CHO + H_2 \xrightarrow{Pd} R-CH_2OH$$

$$RCOR' \xrightarrow{NaBH_4} R-CH(OH)-R$$

$$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R-CH_2-OH$$

From Grignard reagent

$$>C=O + R^{\delta-} + Mg^{\delta+}X \longrightarrow \left[>C(O-Mg-X)\right]$$

$$\xrightarrow{H_2O} Mg(OH)X + >C(OH)-$$

PHYSICAL PROPERTIES

- Soluble in water due to H-bonding
- M.P. and B.P. ∝ Molecular mass M.P. and B.P. ∝
- Colorless with characteristic S Smell

CHEMICAL PROPERTIES

Structure

R-OH

where R = alkyl group

Reaction involving cleavage of -OH bond.

$$Ph-OH + NaOH \longrightarrow Ph-ONa + H_2O$$

Acidity: Due to the presence of polar-OH group.

$$R-CH_2OH \text{ (1° alcohol)} > R-CH(R)-OH \text{ (2° alcohol)} > R-C(R)(R)-OH$$

Esterification

$$R-OH + R'COOH \xrightleftharpoons{H^+} ROCOR' + H_2O$$

$$R-OH + (R'CO)_2O \xrightleftharpoons{H^+} ROCOR' + R'COOH$$

$$R-OH + R'COCl \xrightleftharpoons{Pyridine} ROCOR' + HCl$$

Dehydration Reaction

$$-C(H)-C(OH)- \xrightarrow[Heat]{H^+} >C= + H_2O$$

Oxidation

$$R-CH_2OH \xrightarrow{Oxidation} R-CHO \text{ (Aldehyde)} \xrightarrow{(O)} R-COOH \text{ (Carboxylic Acid)}$$

CHEMICAL TEST FOR ALCOHOL

Victor Mayer Test

Primary Alcohol

$$R-CH_2-OH \xrightarrow[3)\ HNO\ .\ KOH]{1)\ P+I_2,\ 2)\ AgNO} \text{Red Colours}$$

Secondary Alcohol

$$R_2CH-OH \xrightarrow[3)\ HNO\ .\ KOH]{1)\ P+I_2,\ 2)\ AgNO_2} \text{Blue Colours}$$

Tertiary Alcohol

$$R_3C-OH \xrightarrow[3)\ HNO]{1)\ P+I_2,\ 2)\ AgNO} \text{NoReaction} \xrightarrow{KOH} \text{No Colours}$$

PHENOL

METHODS OF PREPARATION OF PHENOL

FROM DIAZONIUM SALTS

$$Ph-NH_2 \text{ (Aniline)} \xrightarrow[HCl]{NaNO_2} Ph-N\equiv NCl \text{ (Benzene Diazonium Salt)} \xrightarrow[warm]{H_2O} Ph-OH + N_2 + HCl$$

FROM BENZENE SUPLHONIC ACID

$$Ph-SO_3H \xrightarrow{Oleum} \xrightarrow[(ii)\ H^+]{(i)\ NaOH} Ph-OH$$

DOW'S PROCESS:

$$\text{Chlorobenzene} \xrightarrow[(ii)\ HCl]{NaOH,\ (i)\ 623\ K,\ 300\ atm} \text{Phenol}$$

FROM CUMENE:

$$\text{Cumene} \xrightarrow{O_2} \text{Cumene Hydroperoxide} \xrightarrow[H_2O]{H^+} Ph-OH + CH_3COCH_3$$

PHYSICAL PROPERTIES

- Colorless crystalline Solid or Liquid
- Higher boiling point due to Hydrogen Bonding

CHEMICAL PROPERTIES

Electrophilic Aromatic Substitution

Halogeneation

$$Ph-OH + 3Br_2 \longrightarrow Ph(OH)(Br)_3 + 3HBr$$

Nitration

$$Ph-OH \xrightarrow[HNO_3]{Conc.\ NO_2} Ph(OH)(NO_2)_3$$

2,4,6-Trinitro-Phenol

Reimer-Tiemann reaction: Treatement of Phenol with $CHCl_3$ + KOH

$$Ph-OH \xrightarrow{CHCl_3 + Aq.\ NaOH} \text{Intermediate} \xrightarrow{NaOH} \xrightarrow{H^+} \text{Salicylaldehyde}$$

Oxidation Phenol

$$Ph-OH \xrightarrow[H_2SO_4]{Na_2Cr_2O_7} \text{Benzoquinone}$$

ETHER

Structure

R-O-R'

where R and R' can be Same or different alkyl group

CHEMICAL PROPERTIES

CLEAVAGE OF C-O BOND

$$R-O-R + HX \longrightarrow R-X + ROH$$

$$R-O-R' + HX \longrightarrow R-X + R'OH$$

$$Ph-OR + H-X \longrightarrow Ph-OH + R-X$$

For Tertiary Group:

$$CH_3-C(CH_3)_2-OCH_3 + HI \rightarrow CH_3OH + CH_3-C(CH_3)_2-I$$

ELECTROPHILIC SUBSTITUTION

(I) HALOGENATION

$$Ph(OCH_3) \xrightarrow{Br_2\ in\ Ethanoic\ Acid} Ph(OCH_3)(Br) + Ph(OCH_3)(Br)$$

(II) FRIEDEL-CRAFTS REACTION

$$Ph(OCH_3) + CH_3Cl \xrightarrow{AlCl_3} Ph(OCH_3)(CH_3) + Ph(H_3C)(CO)$$

PREPARATION OF ETHER

Williamson Synthesis

$$R-X + R-\ddot{O}-Na \longrightarrow R-\ddot{O}-R + NaX$$

By Dehydration of Alcohols

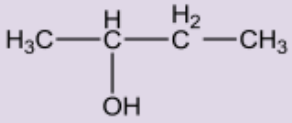
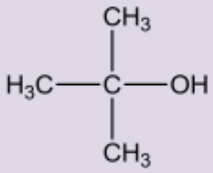
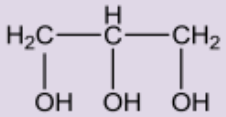
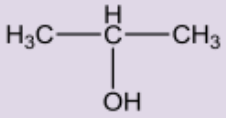
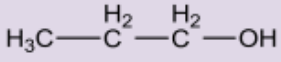
$$2CH_3-CH_2-OH \xrightarrow[413\ K]{H_2SO_4} C_2H_5-O-C_2H_5$$

Alcohols, Phenols and Ethers

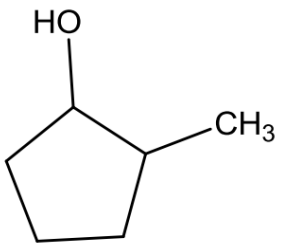
Introduction

- Alcohols and phenols are compounds formed when a hydrogen atom in a hydrocarbon is replaced by–OH group.
- An alcohol contains one or more hydroxyl (OH) group(s) directly attached to carbon atom(s) of analiphatic system.
- A phenol contains –OH group(s) directly attached to carbon atom(s) of an aromatic system (C_6H_5OH).
- The substitution of a hydrogen atom in a hydrocarbon by an alkoxy or aryloxy group (R-O/Ar-O) givesanother class of compounds known as ethers.
  For example:C_2H_5-O-C_2H_5 (Dimethyl ether)

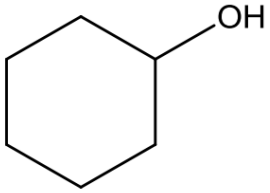
Nomenclature

Compound	Common name	IUPAC name
	*sec*-Butyl alcohol	Butan-2-ol
	*tert*-Butyl alcohol	2-Methylpropan-2-ol
	Glycerol	Propane -1, 2, 3-triol
	Isopropyl alcohol	Propan-2-ol
	*n*-Propyl alcohol	Propan-1-ol

In case of cyclic compounds, we use the prefix cyclo if the –OH group is attached to C-1.

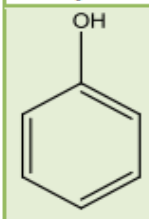
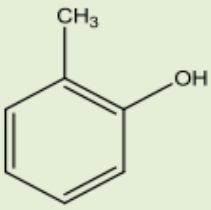
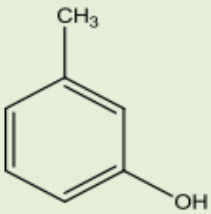
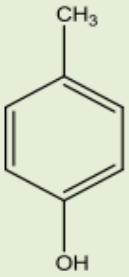
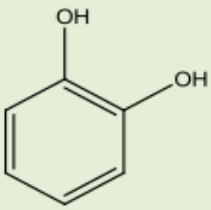
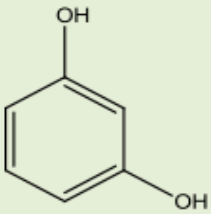
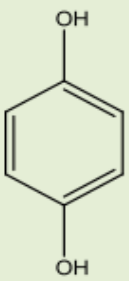


2-Methylcyclopentanol

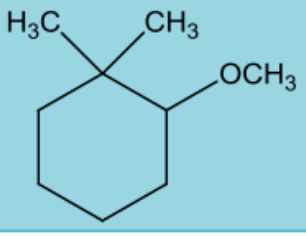


Cyclohexanol

Phenols:

Compound	Common name	IUPAC name
	Phenol	Phenol
	*o*-Cresol	2-Methylphenol
	*m*-Cresol	3-Methylphenol
	*p*-Cresol	4-Methylphenol
	Catechol	Benzene-1,2-diol
	Resorcinol	Benzene-1,3-diol
	Hydroquinone or quinol	Benzene-1,4-diol

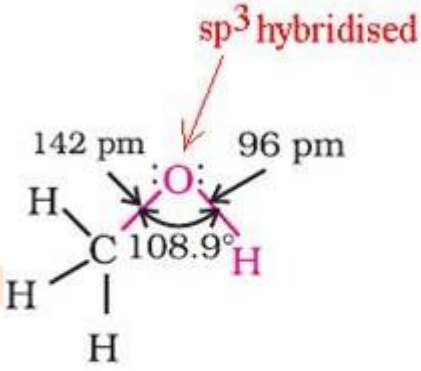
Ethers

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$C_6H_5O(CH_2)_6\text{-}CH_3$	Heptyl phenyl ether	1-Phenoxyheptane
	Phenyl isopentyl ether	3- Methylbutoxybenzene
$C_6H_5\text{-}O\text{-}CH_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$	----	1,2-Dimethoxyethane
$CH_3\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OCH_3$	---	
		2-Ethoxy- -1,1-dimethylcyclohexane

Structures of Functional Groups

Alcohols

- For alcohols, the –OH group is linked to carbon by a sigma bond.
- The bond is formed by the overlap of sp^3 hybridised orbital of carbon with a sp^3 hybridised orbital ofoxygen.



Methanol

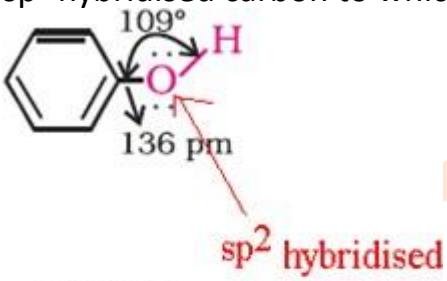
(Alcohol)

- In alcohols, the bond angle is slightly less than the tetrahedral angle (109°-28') due to therepulsion between the unshared electron pairs of oxygen.

Phenols

- In phenols, the –OH group is linked to carbon by sp^2 hybridisation.
- The C-O bond length (136 pm) in phenol is slightly less than that in methanol.

- This arises due to:
  - Partial double bond character on account of the conjugation of unshared electron pair of oxygenwith the aromatic ring.
  - sp^2 hybridised carbon to which oxygen is linked.

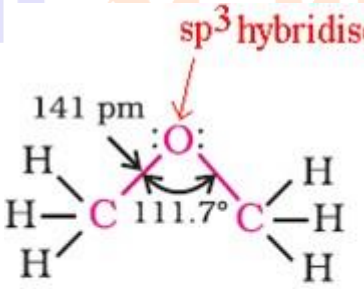


Phenol

(Phenol)

Ethers

- In ethers the two bond pairs and two lone pairs of electrons on oxygen form a tetrahedralarrangement.
- Due to the repulsive interaction between the two bulky (-R) groups the bond angle is slightlygreater than the tetrahedral angle.
- The C-O bond length is almost the same like alcohols.



Methoxymethane

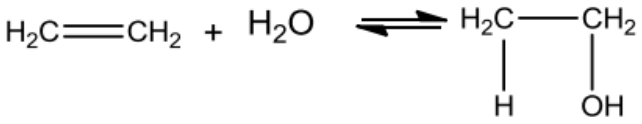
(Ether)

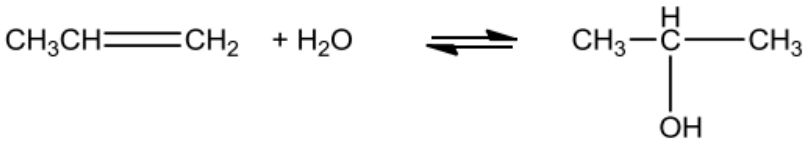
Preparation of Alcohols

From Alkenes

- **Acid catalysed hydration:**

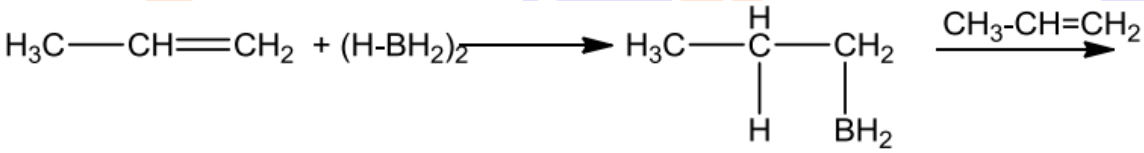
Alcohols are prepared by treating alkenes with water in the presence of acid as catalyst.

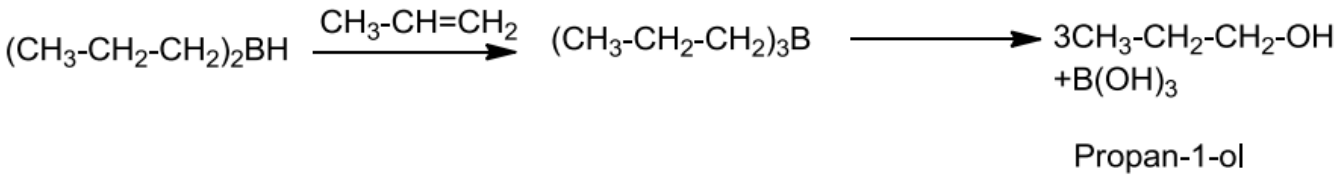




➢ Hydroboration-oxidation:

Alkenes on treatment with diborane give trialkyl boranes as addition product which is then oxidised toalcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.





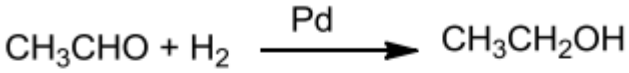
Propan-1-ol

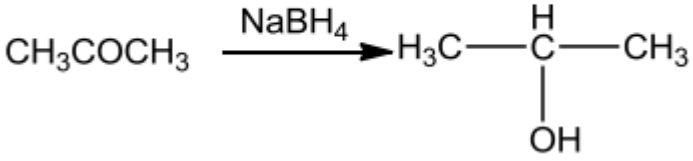
The addition of borane to the double bond takes place in such a way that the boron gets added to thesp^2 carbon with more number of hydrogen atoms.

From Carbonyl Compounds

➢ Reduction of Aldehydes & Ketones

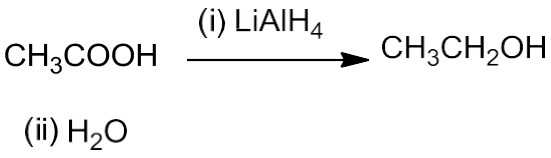
- Aldehydes yield primary alcohols whereas ketones give secondary alcohols.



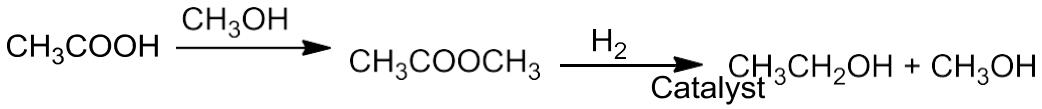


➢ Reduction of Carboxylic acids and Esters

- $LiAlH_4$ is a strong reducing agent and reduces carboxylic acids to primary alcohols in excellent yields.

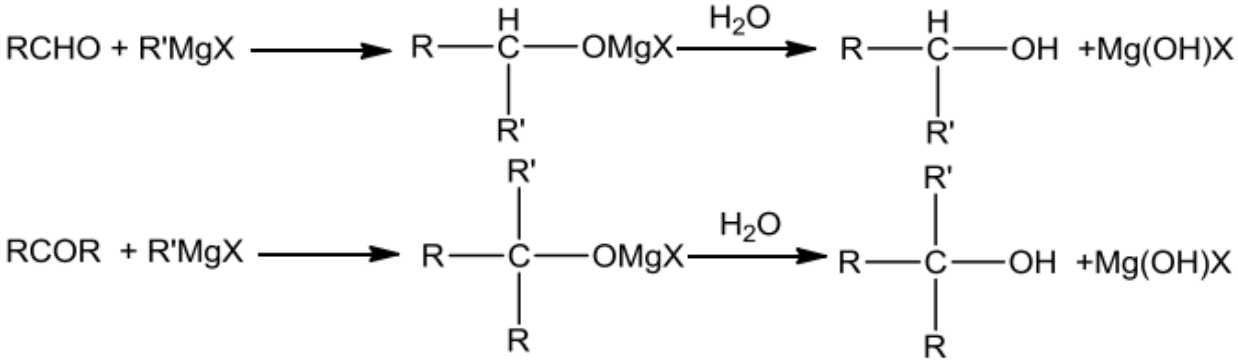


- Alcohols are prepared on a commercial scale by converting acids to esters followed by reduction withhydrogen in the presence of catalyst.



From Grignard reagents

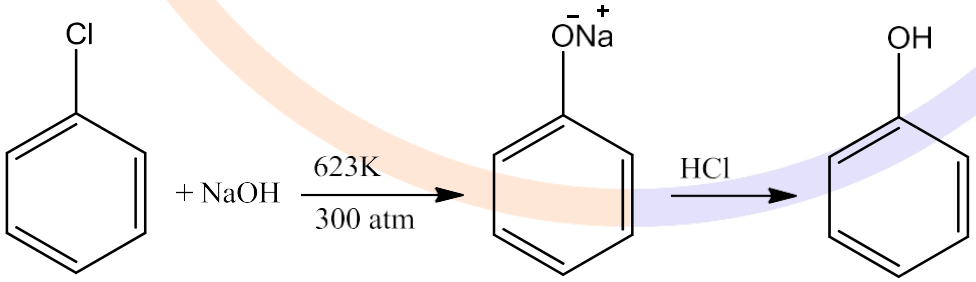
Grignard reagents on reacting with aldehydes and ketones yield alcohols.



Preparation of Phenols

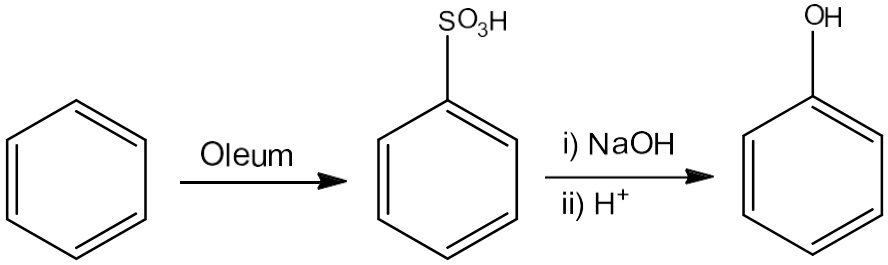
➢ **From Haloarenes**

Chlorobenzene on fusing with NaOH at 623 K and 320 atmospheric pressure gives sodium phenoxidewhich on acidification yields phenol.



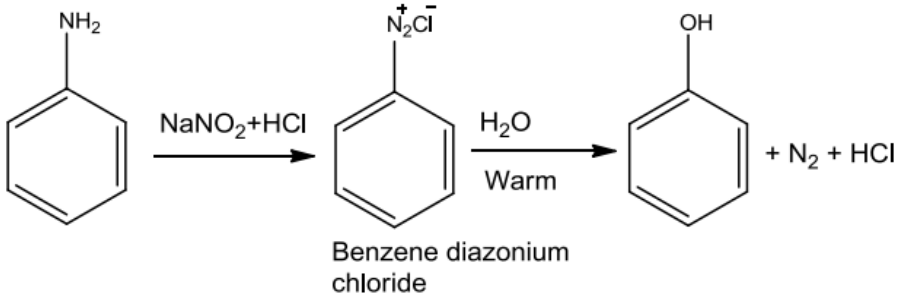
➢ **From Benzenesulphonic Acid**

Benzene on sulphonation with oleum gives benzene sulphonic acid which on heating with moltensodium hydroxide gives sodium phenoxide. Acidification of the sodium phenoxide gives phenol.



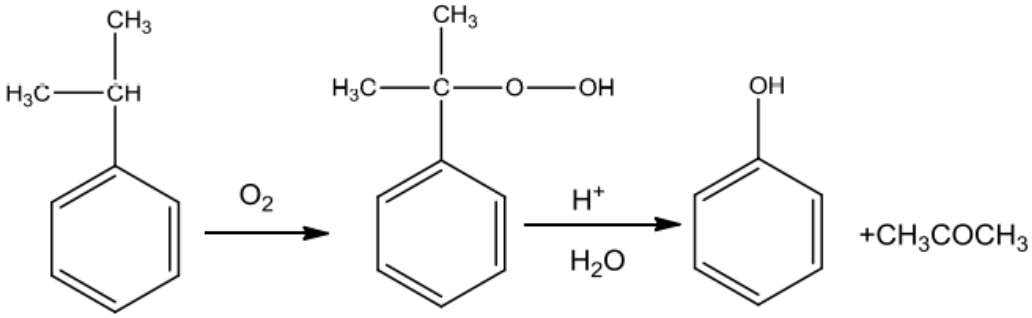
➢ **From Diazonium Salts**

Aniline on treatment with nitrous acid at 273-278K gives benzene diazonium chloride which onhydrolysis with warm water or treatment with dilute acids is converted to phenols.



➢ **From Cumene**

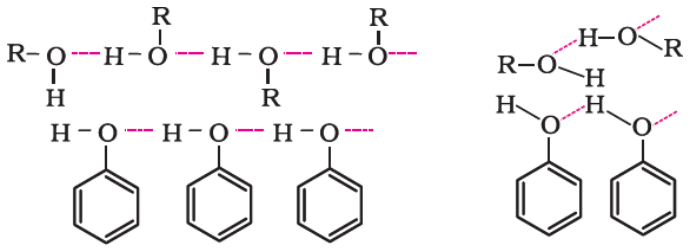
Cumene(isopropylbenzene) on oxidation with air gives cumene hydroperoxide which on treatment withdilute acid is converted to phenol.



Physical Properties

➢ **Boiling points**

- Boiling points of alcohols and phenols are higher in comparison to other classes of compounds, namely hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This isbecause the –OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.

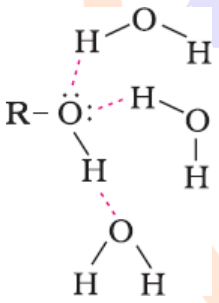


- The boiling points of alcohols and phenols increase with increase in the number of carbon atoms. Thisis because of increase in van der Waals forces with increase in the surface area.

- In alcohols, the boiling points decrease with increase in branching in the carbon chain. This is becauseof decrease in van der Waals forces with decrease in the surface area.

➢ **Solubility**

- Alcohols and phenols are soluble in water due to their ability to form hydrogen bonds with watermolecules.



- The solubility of alcohols decreases with increase in the size of alkyl/aryl (hydrophobic) groups.

Chemical Properties

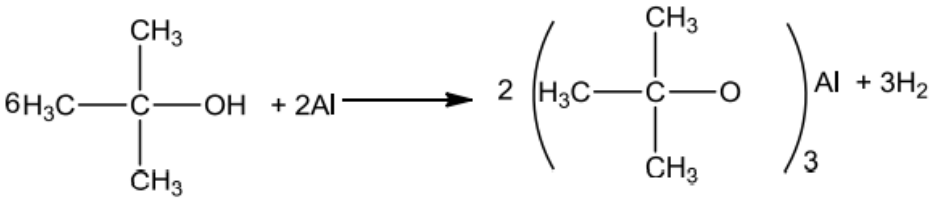
Alcohols react both as nucleophiles and electrophiles.

A) Reactions involving cleavage of O-H bond

(i) Reaction with Metals

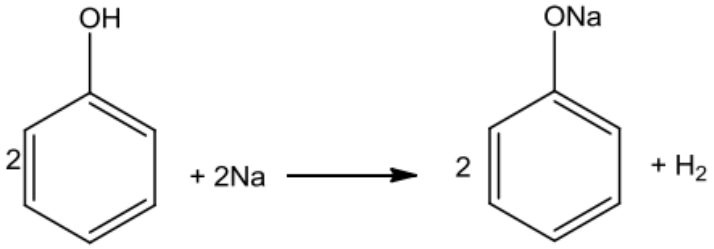
Alcohols and phenols react with active metals like Na, K and Al to give correspondingalkoxides/phenoxides with the evolution of hydrogen.

$2R\text{-}OH + 2Na \rightarrow 2R\text{-}O\text{-}Na + H_2$



tert. -butyl alcohol

Aluminium tert. butoxide

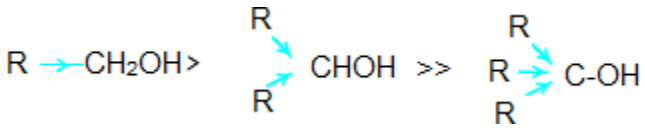


Phenol

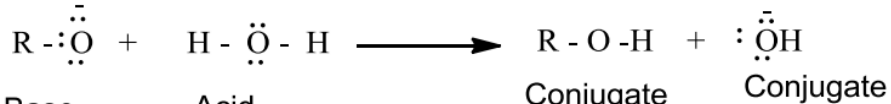
Sodium phenoxide

(ii) Acidity of Alcohols

- The acidity of alcohols depends on the polar nature of O-H bond.
- The electron releasing groups (-CH_3, -C_2H_5) increases the electron density on oxygen andthus decrease the polarity of O-H bond which decreases the acid strength.
- The acid strength of alcohols decreases in the following order:



- Alcohols are weaker acids than water which can be seen in the following reaction.



Base Acid Conjugate acid Conjugate base

In the reaction, water is a better proton donor (i.e., stronger acid) than alcohol. Over herethe alkoxide ion is a better proton acceptor than hydroxide ion which suggests that alkoxides are stronger bases.

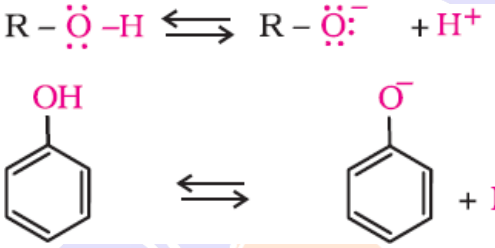
- Alcohols act as Bronsted bases as well due to the presence of unshared electron pairs onoxygen which makes them proton acceptors.

(iii) Acidity of Phenols

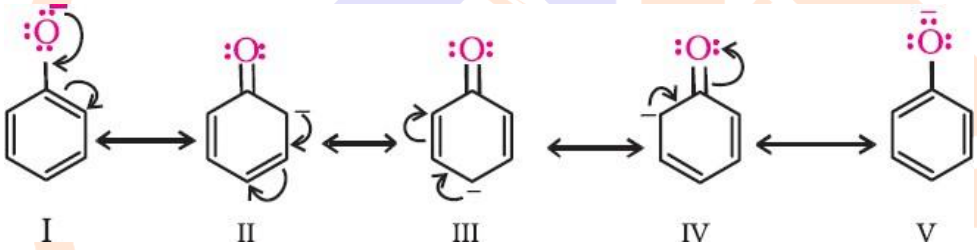
- In phenol, the hydroxyl group is directly attached to the sp^2 hybridised carbon of the benzene ring which acts as an electron-withdrawing group. Whereas in

alcohols, the hydroxyl group is attached to the alkyl group which has an electron-releasing inductiveeffect.

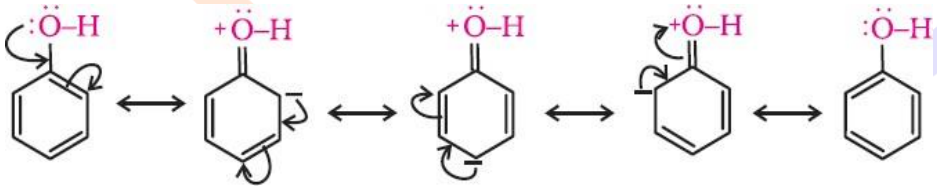
- In phenol, the hydroxyl group is directly attached to the sp^2 hybridised carbon of the benzene ring. Whereas in alcohols, the hydroxyl group is attached to the sp^3 hybridised carbon of the alkyl group. The sp^2 hybridised carbon has higher electronegativity than thesp^3 hybridised carbon. Thus, the polarity of the O–H bond of phenols is higher than that ofalcohols. Hence, the ionisation of phenols is higher than that of alcohols.
- The ionisation of an alcohol and a phenol occurs as follows:



- In alkoxide ion, the negative charge is localised on oxygen, while in phenoxide ion, thecharge is delocalised.



- The delocalisation of the negative charge makes the phenoxide ion more stable and favoursthe ionisation of phenol. Although there is charge delocalisation in phenol, its resonance structures have charge separation due to which the phenol molecule is less stable than the phenoxide ion.



- In substituted phenols, the presence of electron-withdrawing groups such as the nitro groupenhances the acidic strength of phenol. On the other hand, electron-releasing groups, suchas alkyl groups, decrease the acidic strength. It is because electron-withdrawing groups lead to effective delocalisation of the negative charge in the phenoxide ion.

(iv) Esterification

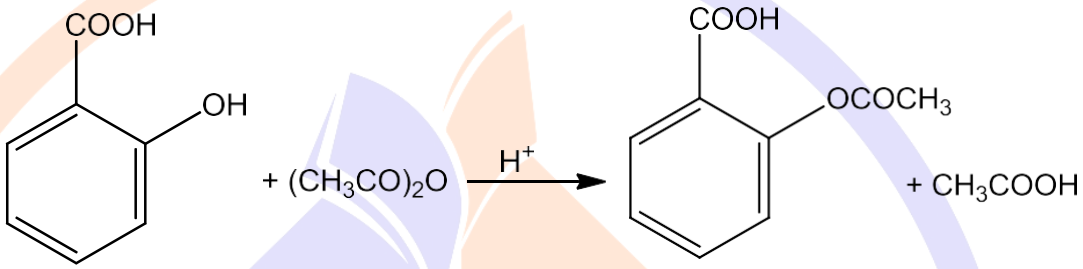
- Esters are formed when alcohols and phenols react with carboxylic acids, acid chloridesand acid anhydrides.

$$Ar/RO\text{-}H + R'\text{-}COOH \xrightleftharpoons{H^+} Ar/ROCOR' + H_2O$$

$$Ar/RO\text{-}H + (R'CO)_2O \xrightleftharpoons{H^+} Ar/ROCOR' + R'COOH$$

$$R/ArOH + R'COCl \xrightarrow{Pyridine} R/ArOCOR' + HCl$$

- In case of acid chloride, the reaction is carried out in the presence of base called pyridine toneutralise the HCl formed and to shift the equilibrium to the right.



Salicylic acid

Acetylsalicylic acid (Aspirin)

B) Reactions involving cleavage of Carbon-Oxygen(C-O) bond in alcohols

Only alcohols show reactions involving cleavage of C-O bond. Phenols exhibit this type of reactiononly with zinc.

i) Reaction with hydrogen halides

Alcohols on treatment with hydrogen halides form alkyl halides.

$ROH + HX \rightarrow R\text{-}X + H_2O$

How to distinguish between Primary, Secondary and Tertiary Alcohols?

Lucas reagent test

$$ROH + HCl \xrightarrow[\text{Lucas reagent}]{\text{conc.HCl} + ZnCl_2} RCl + H_2O$$

- If it is a primary alcohol, then no turbidity appears at room temperature. Turbidity appears onlyon heating.
- If it is a secondary alcohol, then turbidity appears in 5 minutes.
- If it is a tertiary alcohol, then turbidity appears immediately.

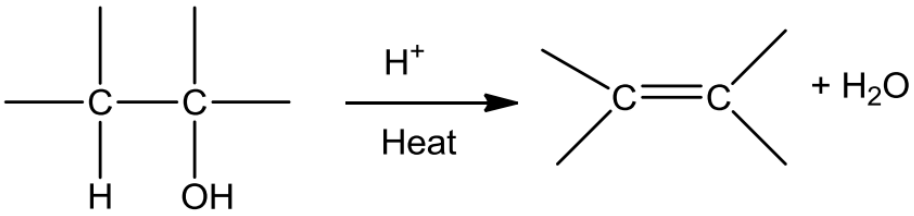
ii) Reaction with Phosphorus trihalides

Alcohols get converted into alkyl bromides on treatment with PBr_3.

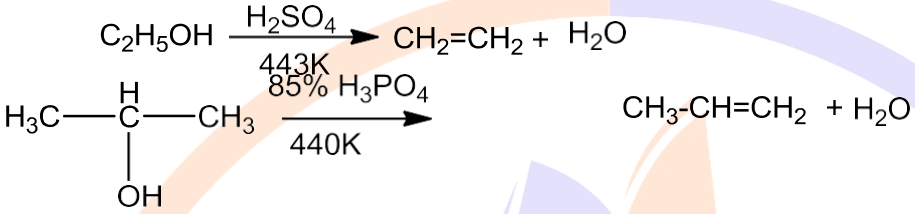
$3R\text{-}OH + PBr_3 \rightarrow 3R\text{-}Br + H_3PO_3$

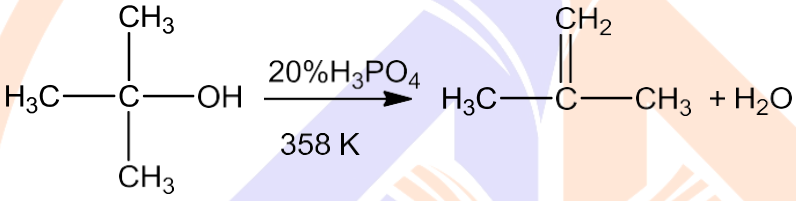
iii) Dehydration

- Alcohols undergo dehydration to form alkenes in the presence of conc. H_2SO_4 or H_3PO_3 orcatalysts such as anhydrous zinc chloride or alumina.



- Primary alcohol undergoes dehydration by heating it with conc. H_2SO_4 at 443K.
- Secondary and tertiary alcohols undergo dehydration in milder conditions.

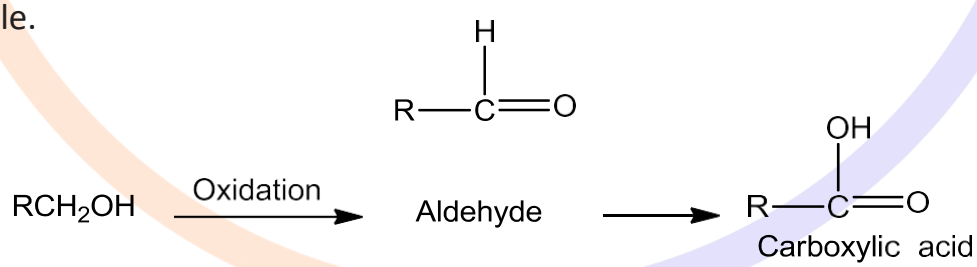




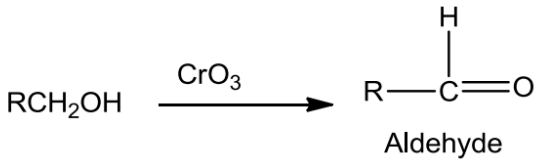
- Thus the ease of dehydration of alcohols follows the order:
  Tertiary > Secondary > Primary

iv) Oxidation

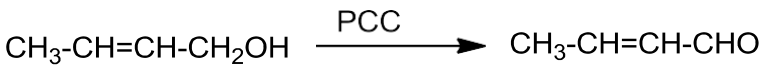
- The oxidation of alcohols results in the formation of a carbon-oxygen double bond with the cleavage of an O-H and C-H bonds. The reaction is known as dehydrogenation reaction as it involves loss of dihydrogen from an alcohol molecule.



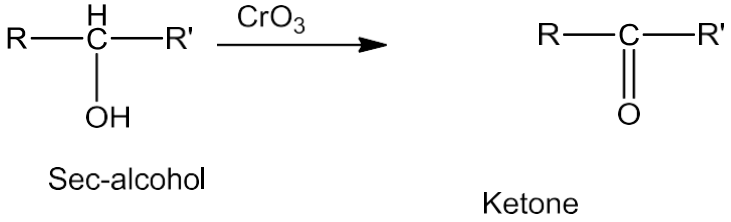
- Use of strong oxidising agents like acidified $KMnO_4$ is done to obtain carboxylic acids from alcohols directly. CrO_3 in anhydrous medium is used for obtaining aldehydes.



- Pyridinium chlorochromate (PCC), a complex of chromium trioxide with pyridine and HCl isa better oxidizing agent for oxidation of primary alcohols to aldehydes in good yield.



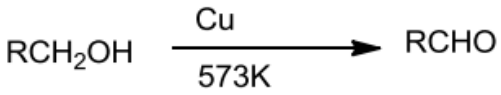
- CrO_3 is used to oxidize secondary alcohols to ketones.

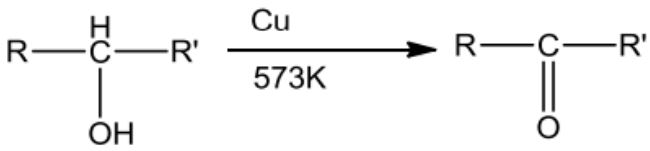


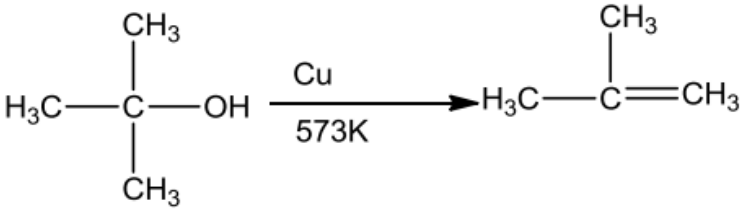
Sec-alcohol

Ketone

- Tertiary alcohols do not undergo oxidation reaction. In presence of strong oxidizing agents($KMnO_4$) and elevated temperatures, cleavage of C-C bonds takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.
- On passing vapours of a primary or a secondary alcohol over heated copper at 573K, dehydrogenation takes place and an aldehydes or a ketone is formed whereas tertiaryalcohols undergo dehydration.





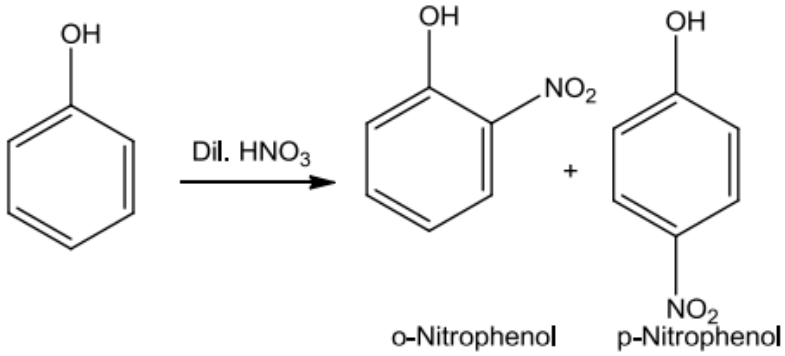


Characteristics of Phenols

- Phenols show electrophilic substitution reactions.
- The –OH group activates the benzene ring towards electrophilic substitution and also directs the incoming group to ortho and para positions in the ring as these positions become electron rich due tothe resonance effect caused by –OH group.

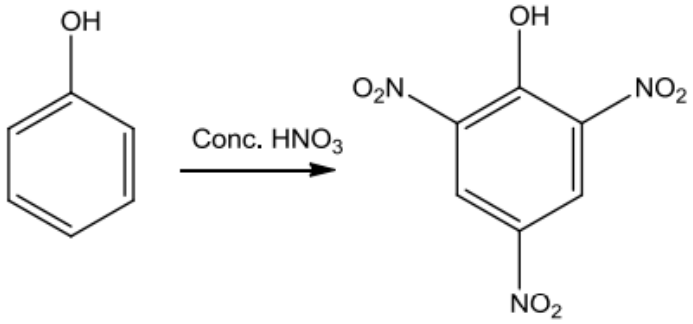
(i) Nitration

Phenol on treatment with dil.HNO_3 at low temperature yields a mixture of ortho and para nitrophenols.



o-Nitrophenol p-Nitrophenol

With conc. nitric acid, phenol is converted into 2, 4, 6-trinitrophenol.

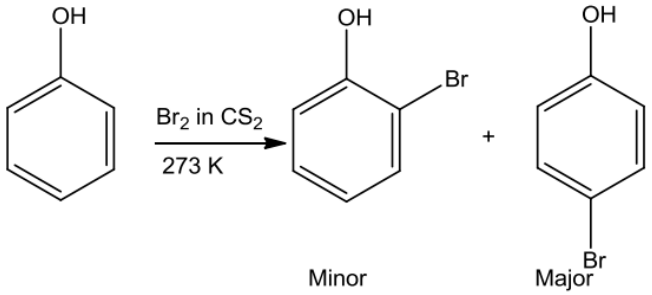


2,4,6-Trinitrophenol
(Picric acid)

(ii) Halogenation

(a) Bromine in $CHCl_3$ or CS_2

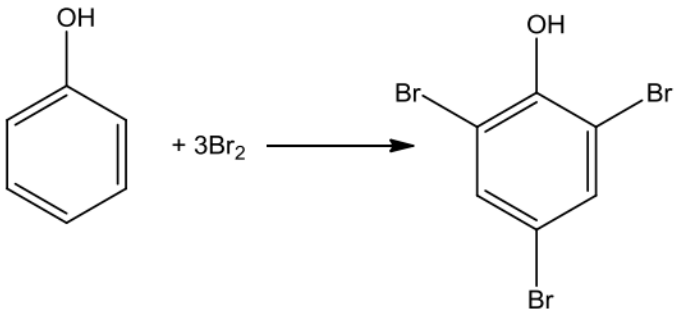
Monobromophenols are formed when phenol is treated with bromine in $CHCl_3$ or CS_2 at lowtemperature.



Minor Major

(b) Action of Bromine water

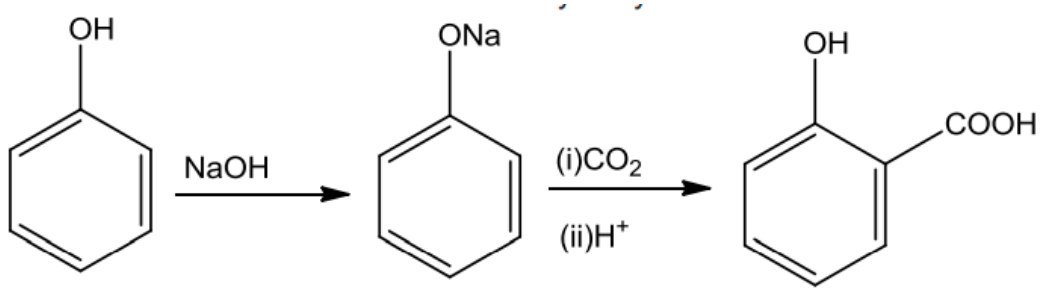
On treating phenol with bromine water, a white precipitate of 2, 4, 6-tribromophenol is formed.



2,4,6-Tribromophenol

(iii) Kolbe's Reaction

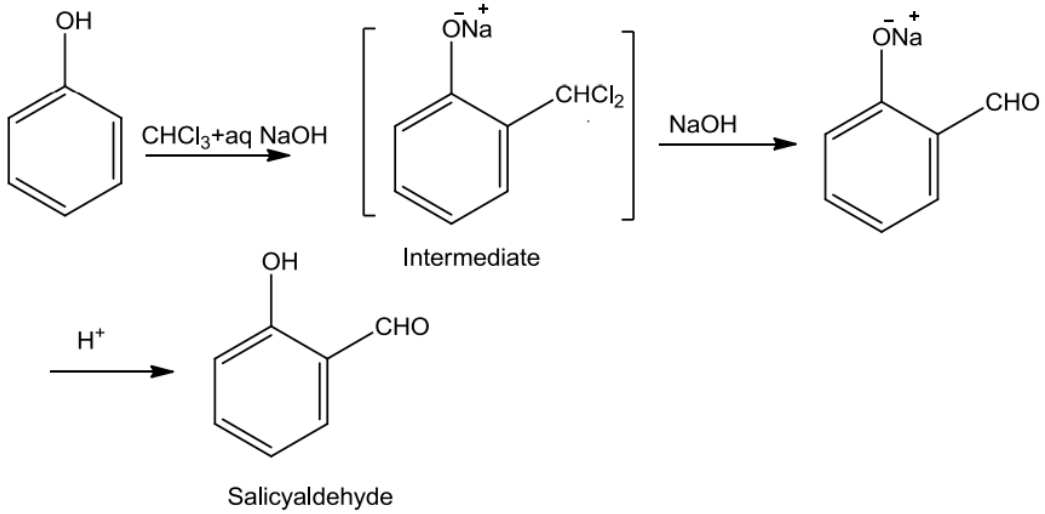
Phenols on treatment with NaOH produces phenoxide ion which is even more reactive than phenol towards electrophilic aromatic substitution and therefore it undergoes electrophilic substitution with carbon dioxide. Ortho hydroxybenzoic acid is obtained as the main product.



2-Hydroxybenzoic acid
(Salicylic acid)

(iv) Reimer-Tiemann Reaction

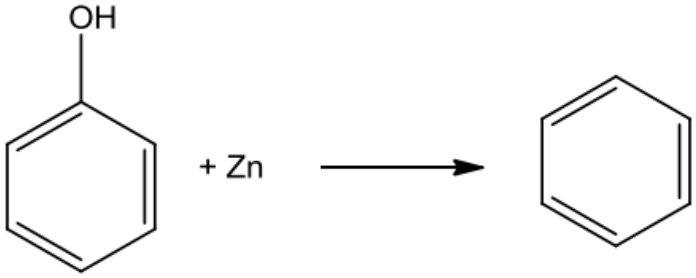
Phenols on treatment with chloroform in the presence of NaOH, a –CHO group is introduced atortho position of benzene ring. The substituted benzal chloride formed as intermediate on hydrolysis with alkali produce salicylaldehyde.



Salicyaldehyde

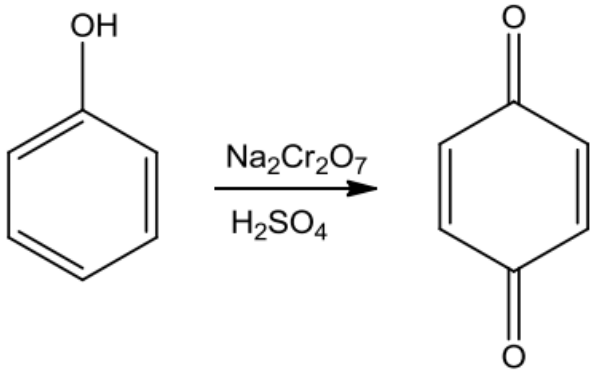
(v) Action of Zinc dust

Phenol on heating with zinc dust produces benzene.



(vi)Oxidation

Phenols on oxidation with chromic acid gives out conjugated diketone known as benzoquinone.



Some Commercially Important Alcohols

Methanol and ethanol are two commercially important alcohols.

Methanol

- Methanol also known as 'wood spirit' was produced by destructive distillation of wood.
- Now methanol is produced by catalytic hydrogenation of carbon monoxide at high pressure andtemperature in the presence of $ZnO\text{-}Cr_2O_3$ catalyst.

$$CO + 2H_2 \xrightarrow[200\text{-}300\ atm,\ 573\text{-}673K]{ZnO\text{-}Cr_2O_3} CH_3OH$$

Ethanol

- It is commercially obtained by fermentation from sugars.
- The sugar in molasses, sugarcane or fruits like grapes is converted to glucose and fructose in thepresence of an enzyme invertase.
- Glucose and fructose undergo fermentation in the presence of another enzyme, zymase, which isfound in the yeast.

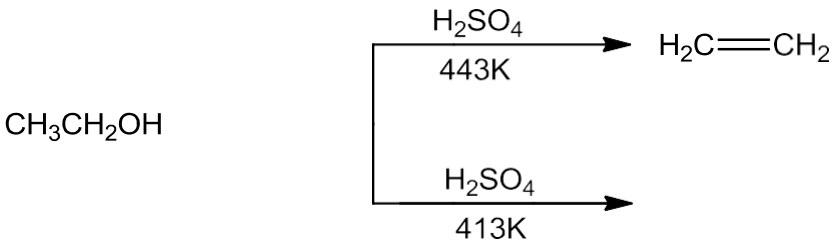
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$$

Preparation of Ethers

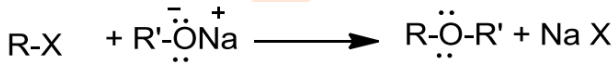
➢ By Dehydration of Alcohols

- Alcohols on dehydration with protic acids like H_2SO_4, H_3PO_4 give alkene or ether depending on thereaction conditions.

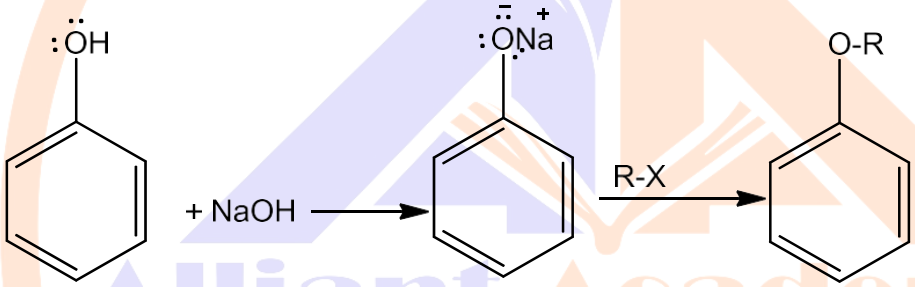


➢ Williamson Synthesis

- This method is used for the preparation of symmetrical and unsymmetrical ethers.
- In this reaction, an alkyl halide is allowed to react with sodium alkoxide.



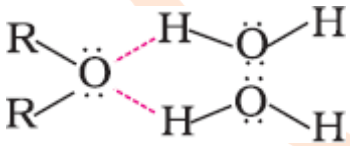
- Phenols can also be converted into ethers using this method. In this, phenol is used as thephenoxide moiety.



Physical Properties of Ethers

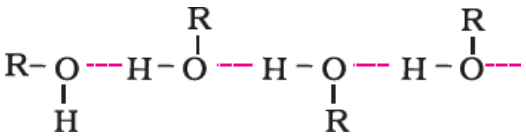
➢ Miscibility

Miscibility of ethers with water resembles those of alcohols of the same molecular mass. This is because similar to alcohols; oxygen of ether can also form hydrogen bonds with the water molecule.



➢ Boiling points

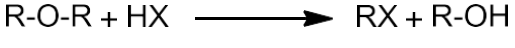
Ethers have much lower boiling points than alcohols. This is due to the presence of hydrogen bondingin alcohols. Hydrogen bonding is absent in ethers.



Chemical Properties of Ethers

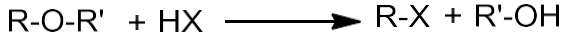
A. Cleavage of C–O bond in ethers

- Since ethers are least reactive of the functional groups, the cleavage of C-O

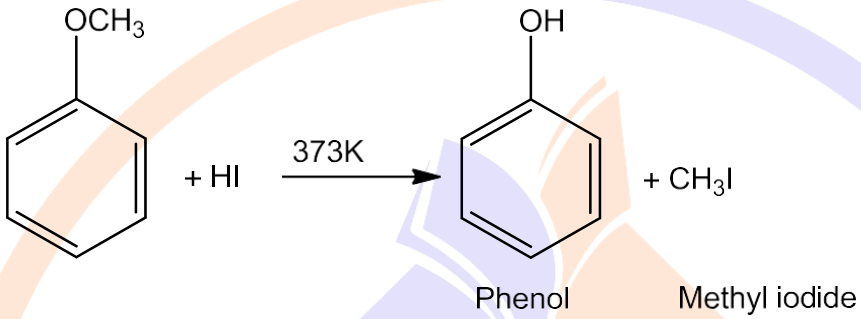


bond in etherstakes place in excess of hydrogen halides.

- The cleavage of ethers with two different alkyl groups also takes place in the same manner.

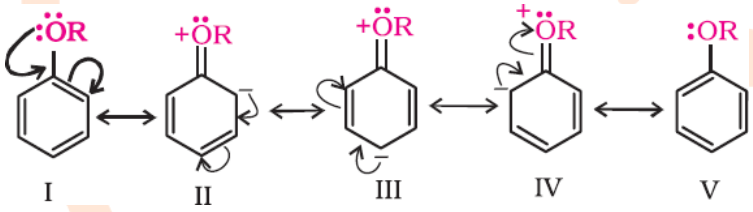


- In phenolic ethers, the cleavage occurs with the formation of phenol and alkyl halide.

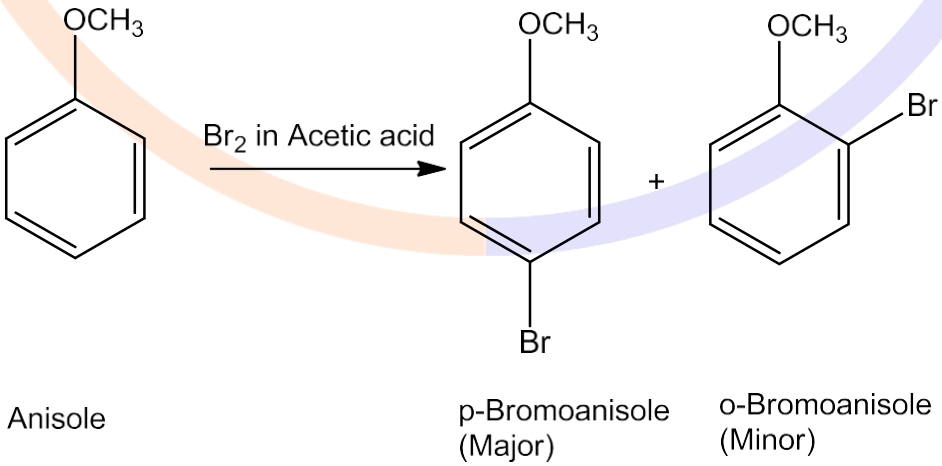


B. Electrophilic Substitution

The alkoxy group (-OR) is ortho, para directing and activates the benzene ring for aromatic substitution.



(i) Halogenation

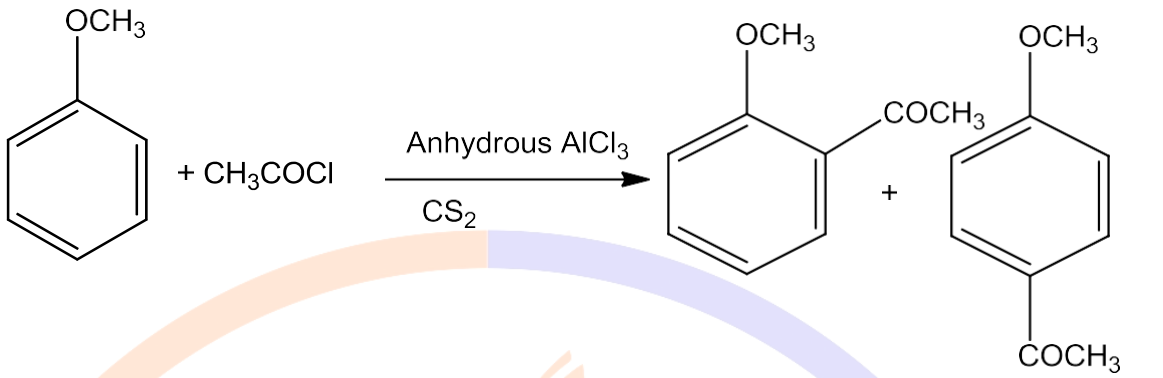


Phenyl alkyl ethers undergo halogenation reaction.

(ii) Friedel-Crafts reaction

In this reaction the alkyl groups and acyl groups are introduced at ortho and para position by treating anisole with alkyl halide and acyl halide in the presence of

anhydrous chloride ascatalyst.



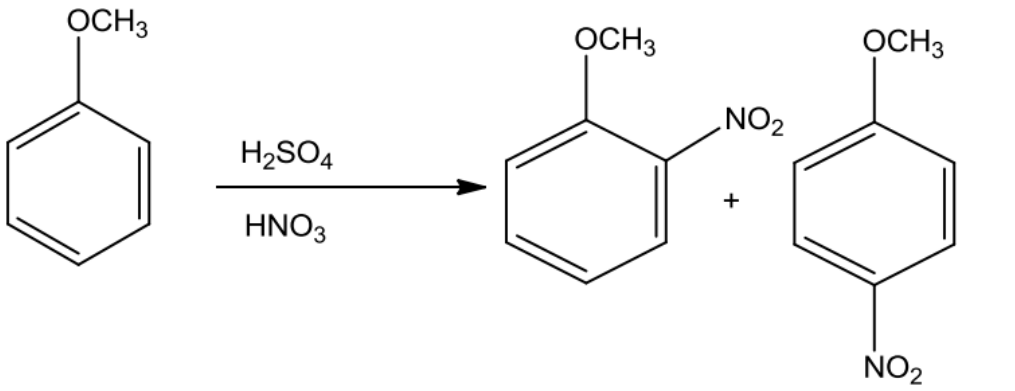
Anisole

2-Methoxy acetophenone

4-Methoxy acetophenone

(iii) Nitration

Anisole on treating with a mixture of sulphuric acid and nitric gives a mixture of ortho andpara nitroanisole.



Anisole

2-Nitroanisole (Minor)

4-Nitroanisole (Major)

NCERT LINE BY LINE QUESTIONS

(1.) **Assertion**: Both symmetrical and unsymmetrical ethers can be prepared by Williamson's synthesis.
Reason: Williamson's synthesis is an example of nucleophilic substitution reaction. [Page: 347]

(a.) Both A and R are true and R is correct explanation of A.
(b.) Both A and R are true but R is not correct explanation of A.
(c.) A is true but R is false.
(d.) Both A and R are false.

(2.) **Assertion**: Alcoholic fermentation involves conversion of sugar into ethyl alcohol by yeast.
Reason: Fermentation involves the slow decomposition of complex organic compounds into simpler substances through complex nitrogenous compounds called enzymes. [Page: 344]

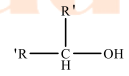
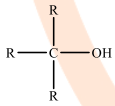
(a.) Both A and R are correct and R is correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

(3.) o-nitrophenol is steam volatile due to [Page: 341]

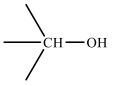
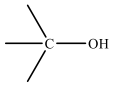
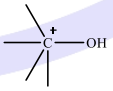
(a.) van der Waal's forces of attraction
(b.) London forces of attraction
(c.) intermolecular H-bonding
(d.) intramolecular H-bonding

(4.) The product obtained in the following reaction is [Page: 331]

$$RCOR + R'MgX \longrightarrow \xrightarrow{H_2O} \text{'Y'} + Mg(OH)_2$$

(a.) RCH_2OH
(b.) 
(c.) 
(d.) None of these

(5.) Which of the following is a tertiary alcohol? [Page: 324]

(a.) $-CH_2OH$
(b.) 
(c.) 
(d.) 

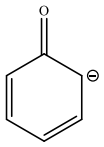
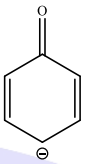
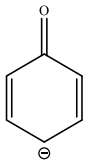
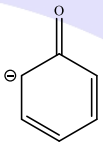
(6.) Reaction of phenol with chloroform in the presence of dilute sodium hydroxide finally introduces, which one of the following functional group? [CBSE AIPMT 2015, Page: 343]

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

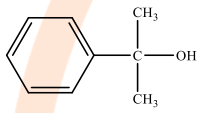
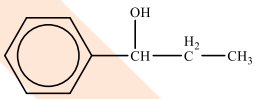
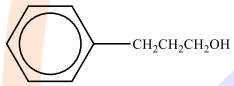
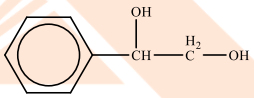
(7.) Consider the following steps involved in the mechanism of acid catalysed hydration. [Page: 329]
(A) Nucleophilic attack of H_2O on carbocation
(B) Protonation of alkene to form carbocation
(C) Deprotonation to form an alcohol
The correct sequence of reaction mechanism is

(a.) A, B, C
(b.) C, B, A
(c.) B, A, C
(d.) A, C, B

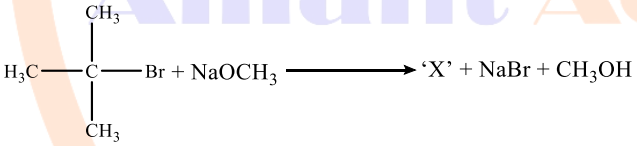
(8.) Which of the following resonating structure of phenol is incorrect? [Page: 336]

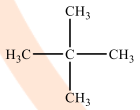
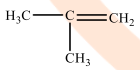
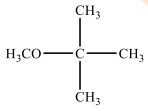
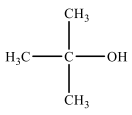
(a.) 
(b.) 
(c.) 
(d.) 

(9.) An alcohol of formula $C_9H_{12}O$ **(A)** reacts with $Na_2Cr_2O_7$ to form a compound having formula $C_9H_{10}O$. The original alcohol might be

(a.) 
(b.) 
(c.) 
(d.) 

(10.) The product in the following reaction is [Page: 346]



(a.) 
(b.) 
(c.) 
(d.) 

(11.) Which of the following statement is correct? [Page: 326-327]

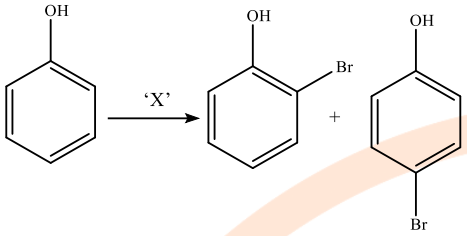
(a.) The simplest hydroxy derivative of benzene is 2-methylphenol.
(b.) In case of phenol, the substituted compounds are termed as ortho, meta and para.
(c.) Trihydroxy derivatives of benzene are known as 1,2-, 1,3- and 1,4-benzenediol.
(d.) In case of ethers, alkyl or aryl groups are written in alphabetical order and adding the word ether.

(12.) Alcohols readily react both as [Page: 334]

(a.) electrophiles (b.) nucleophiles

(c.) Both (a) and (b) (d.) None of these

(13.) Reagent used for following reaction is [Page: 342]



(a.) Br_2 in CS_2 (b.) Br_2 in CCl_4

(c.) Br_2 in CS_2, 273 K (d.) Br_2/water

(14.) Toluene of mono chlorination in presence of sunlight followed by hydrolysis in presence of aq. NaOH yields [NCERT Exemplar, Page: 332]

(a.) 2,4-dihydroxy toluene (b.) benzyl alcohol

(c.) o-cresol (d.) m-cresol

(15.) **Assertion**: CH_3OH undergoes faster esterification than $(CH_3)_3COH$.
Reason: The reaction between an acid and alcohol in presence of dry HCl gas to give ester is known as esterification process. [Page: 337]

(a.) Both A and R are correct and R is correct explanation of A. (b.) Both A and R are correct but R is not correct explanation of A.

(c.) A is correct but R is incorrect. (d.) Both A and R are false.

(16.) Which of the following is not an electrophilic substitution reaction? [Page: 349]

(a.) Nitration (b.) Friedel–Crafts reaction

(c.) halogenation (d.) Williamson synthesis

(17.) The given alcohol is $CH_2 = CH - OH$ is [Page: 325]

(a.) vinylic alcohol (b.) allylic alcohol

(c.) benzylic alcohol (d.) alkylic alcohol

(18.) Which of the following is a 'wood spirit'? [Page: 344]

(a.) Ethanol (b.) Propanol

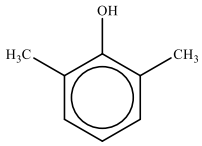
(c.) Methanol (d.) Butanol

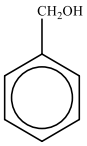
(19.) Consider the following statements: [Page: 337]
(I) In phenol, higher electronegativity of sp2 hydridised carbon to which –OH is attached.
(II) In alkoxide ion, positive charge is localised on oxygen.
(III) In phenoxide ion, the charge is delocalized.
Choose the correct option:

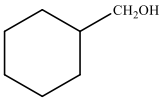
(a.) only I (b.) only III

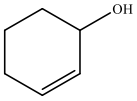
(c.) only I and III (d.) I, II and III

(20.) The correct structure formula for vinylic phenol is

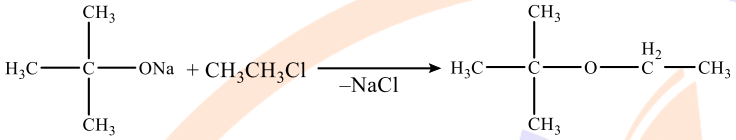
(a.) 

(b.) 

(c.) 

(d.) 

(21.) The reaction [Page: 346, CBSE AIPMT-2015]



is called

(a.) Williamson synthesis

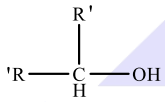
(b.) Williamson continuous etherification process

(c.) Etard reaction

(d.) Gattermann–Koch reaction

(22.) Consider the following reaction [Page: 330]

$RCOR' \xrightarrow{NaBH_4} "Y"$

(a.) 

(b.) RCH_2OH

(c.) $R'CH_2OH$

(d.) RCHO

(23.) Ordinary spirit used for polishing wooden furniture contains [Page: 323]

(a.) Methanol

(b.) Propanol

(c.) Ethanol

(d.) Butanol

(24.) The carbon–oxygen bond length in phenol is slightly less than that in methanol. This is due to [Page: 328]

(a.) partial double bond character on account of conjugation

(b.) sp2 hydridised state of carbon to which oxygen is attached

(c.) Both (a) and (b)

(d.) None of these

(25.) Which of the following group decreases the acidic strength? [Page: 335]

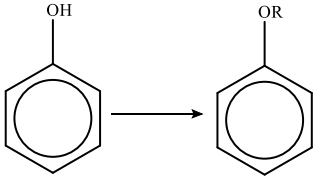
(a.) $-NO_2$

(b.) $-OCH_3$

(c.) $-C_2H_5$

(d.) $-CN$

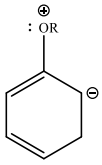
(26.) Consider the following reaction: [Page: 347]

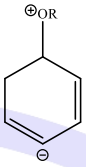


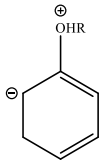
The reagents used to carry out the conversion is

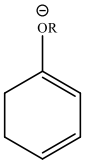
(a.) NaCl, R H
(b.) NaOH, ROH
(c.) NaOH, R X
(d.) NaCl, R F

(27.) The incorrect resonating structure is

(a.) 

(b.) 

(c.) 

(d.) 

(28.) Which of the following statement is wrong?

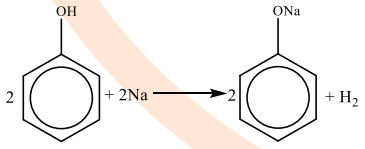
(a.) When diethyl ether is treated with excess Cl_2 in light, perchlorodiethyl ether is obtained $(C_2Cl_5)_2O$.
(b.) When diethyl ether is treated wioth 1mol of Cl_2 in dark, 1-chloroethyl ether is obtained.
(c.) When diethyl ether is treated with 2 mol of Cl_2 in dark, 1,1′-dichlorodiethyl is obtained.
(d.) When diethyl ether is treated with 2 mol of Cl_2 in dark, 1,1′-dichloro and 1,2-dichloro ethyl ether is obtained.

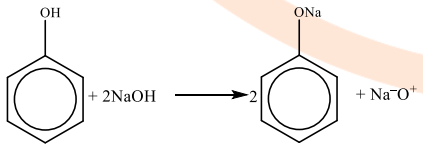
(29.) Which reagent is used to distinguish three classes of alcohols? [Page: 338]

(a.) Br_2/water test
(b.) oxidation
(c.) Lucas test
(d.) none of these

(30.) Which of the following reaction is correct? [Page: 335]

(a.) $2R-O-H \ + \ 2Na \longrightarrow 2R-ONa \ + \ H_2$

(b.) 

(c.) 

(d.) $(CH_3)C-OH \ + \ 2Al \longrightarrow 3\left(\left(CH_3\right)_3 C-O-\right)_3 -Al+3H_2$

(31.) **Assertion**: Di-tert-butyl ether cannot be prepared by Williamson's synthesis.
Reason: tert-butyl bromide on treatment with sodium tert-butoxide preferentially undergoes elimination to form isobutylene and tert-butyl alcohol. [Page: 347]

(a.) Both A and R are true and R is correct explanation of A.
(b.) Both A and R are true but R is not correct explanation of A.
(c.) A is true but R is false.
(d.) Both A and R are false.

(32.) **Assertion**: Tertiary alcohols give turbidity immediately with Lucas reagent.
Reason: A mixture of conc. HI and anhydrous $CuCl_2$ is called Lucas reagent. [Page: 338]

(a.) Both A and R are correct and R is correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

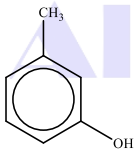
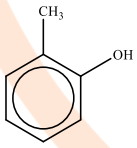
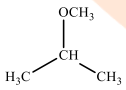
(33.) **Assertion**: $(CH_3)_3C$ Br and $CH_3CH_2O^-$ Na^+ react to form $(CH_3)_3C$ O CH_2CH_3.
Reason: Good yields of ethers are obtained when tert alkyl halides are treated with alkoxides. [Page: 347]

(a.) Both A and R are true and R is correct explanation of A.
(b.) Both A and R are true but R is not correct explanation of A.
(c.) A is true but R is false.
(d.) Both A and R are false.

(34.) **Assertion**: The oxygen of $-OH$ group in alcohols is attached to sp^3 hydridised carbon.
Reason: The bond angle in alcohols $C-OH$ is 109°28′. [Page: 328]

(a.) Both A and R are correct and R is the correct explanation of A.
(b.) Both A and R are correct and R is not correct explanation A.
(c.) A is incorrect; R is correct.
(d.) R is incorrect; A is correct.

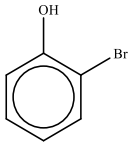
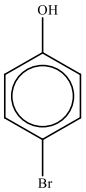
(35.) Match of the following. [NCERT Exemplar, Page: 327]

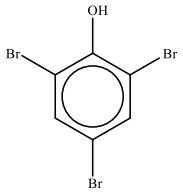
Column I	Column II
(Compound)	(Name)
(I) 	p. 2-methoxypropane
(II) 	q. o-cresol
(III) 	r. m-cresol

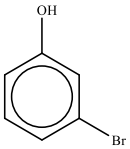
Codes

	I	II	III
(a.)	p	q	r
(b.)	r	q	p
(c.)	r	p	q
(d.)	q	r	p

(36.) When phenol is treated with Br_2 water, 'X' is formed as white precipitate. Hence 'X' is [Page: 342]

(a.) 
(b.) 

(c.) 

(d.) 

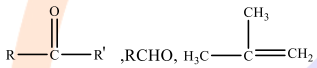
(37.) The –OH group in alcohols and phenols is involved in [Page: 333]

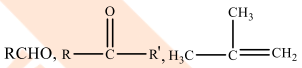
(a.) van der Waal forces of attraction
(b.) intermolecular H-bonding
(c.) intramolecular H-bonding
(d.) London forces of attraction

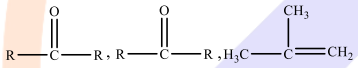
(38.) A compound is soluble in conc. H_2SO_4. It does not decolourise bromine in CCl_4 but oxidised by chromic anhydride in aq. H_2SO_4 within two seconds, turning orange solution to blue green then opaque. The original solution contain

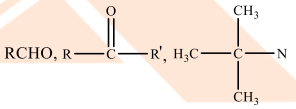
(a.) secondary alcohol
(b.) an alkene
(c.) an ether
(d.) a primary alcohol

(39.) Consider the following reactions: [Page: 340]

(a.) 

(b.) 

(c.) 

(d.) 

(40.) The correct structure of phenyl isopentyl ether is [Page: 327]

(a.) $CH_3OCH_2CH_2OCH_3$
(b.) $C_6H_5O(CH_2)_6CH_3$
(c.) $C_6H_5OCH_2CH_2CHCH_3CH_3$
(d.) $C_6H_5OCH_2CH_3$

(41.) **Assertion**: The boiling point of alcohols are in the order t-butyl alcohol > s-butyl alcohol > n-butyl alcohol.
Reason: The difference between boiling points of two consecutive members of alcohols is about 50–60 K. [Page: 333]

(a.) Both A and R are correct and R is correct explanation of A.
(b.) Both A and R are correct but R is not correct explanation of A.
(c.) A is correct but R is incorrect.
(d.) Both A and R are false.

(42.) Consider the following compounds: [Page: 333]
Pentanol, butanol, ethanol, methanol
I II III IV
The correct increasing order of boiling point is

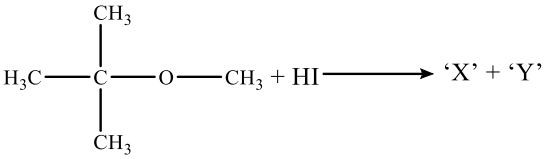
(a.) II > IV < I < III
(b.) IV < II < III < I
(c.) IV < III < II < I
(d.) III < IV < I < II

(43.) Consider the following steps involved in the dehydration of ethanol: [Page: 339]
A. Formation of protonated alcohol
B. Formation of ethene by elimination of a proton.
C. Formation of carbocation. Arrange the given steps:

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

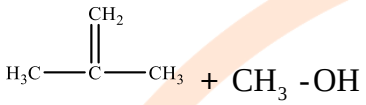
(c.) A, C, B (d.) C, A, B

(44.) Consider the following reaction[Page: 348, HOTS]

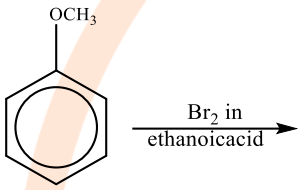


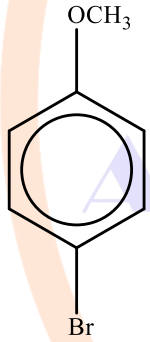
Here, X and Y respectively are

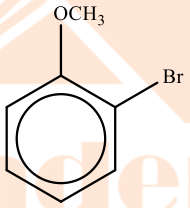
(a.) $CH_3I + (CH_3)_3C - OH$ a (b.) $CH_3OH + (CH_3)_3C - I$

(c.)  (d.) $H_3C - CH_2 - CH_3 + CH_3 - I$

(45.) Product obtained in the following reaction [Page: 349]



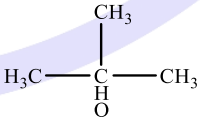
(a.) 

(b.) 

(c.) Both (a) and (b) (d.) None of these

(46.) Compound A ($C_4H_{10}O$) is found to be soluble in concentrated sulphuric acid **(A)** does not react with sodium metal or $K_2C_2O_3$. When **(A)** is heated with excess of HI, it gives a single alkyl halide. The structure of compound. A is

(a.) $CH_3OCH_2CH_2CH_3$

(b.) 

(c.) $CH_3CH_2OCH_2CH_3$ (d.) $CH_3CH_2OCH{=}CH_3$

(47.) The order of reactivity of hydrogen halides with ether is [Page: 347]

(a.) HI > HBr > HCl (b.) HBr > HI > HCl

(c.) HI > HCl > HBr (d.) HI > HBr > HCl

(48.) The reagent used for the following reaction is [Page: 344, HOTS]

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{X} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

Here, 'X' is

(a.) Zymase (b.) Invertase

(c.) Lypase (d.) Protease

(49.) On treating phenol with chloroform in the presence of sodium hydroxide, a CHO group is introduced at ortho position of benzene ring. This reaction is known as [Page: 343]

(a.) Kolbe's reaction (b.) Reimer–Tiemann reaction

(c.) Oxidation (d.) Halogenation

(50.) Consider the following compounds:

Pentane (I) Pentane-1,2,3-triol (II) Butanol (III)

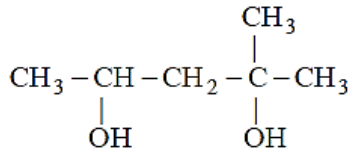
The decreasing order of boiling point and solubility in H_2O is

(a.) II > III > I (b.) III > II > I

(c.) I > II > III (d.) II > I > III

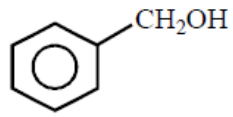
TOPIC WISE PRACTICE QUESTIONS

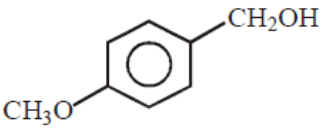
TOPIC 1: General Characteristics of Alcohols, Phenols and Ethers

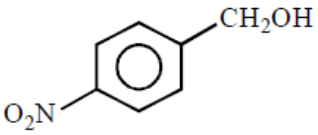
1. Which of the following is dihydric alcohol?
   1) Glycerol 2) Ethylene glycol 3) Catechol 4) Resorcinol
2. The IUPAC name of  is :
   1) 1, 1-dimethyl-1, 3-butanediol 2) 2-methyl-2, 4-pentanediol
   3) 4-methyl-2, 4-pentanediol 4) 1, 3, 3-trimethyl-1, 3-propanediol
3. An example of a compound with functional group – O – is :
   1) acetic acid 2) methyl alcohol 3) diethyl ether 4) acetone
4. Alcoholic beverages contain
   1) isopropyl alcohol 2) *n*-propyl alcohol 3) ethyl alcohol 4) methyl alcohol
5. The C–O–H bond angle in ethanol is nearly
   1) 90° 2) 104° 3) 120° 4) 180°
6. Butane-2-ol is
   1) primary alcohol 2) secondary alcohol 3) tertiary alcohol 4) aldehyde
7. Cresol has
   1) Alcoholic – OH 2) Phenolic – OH 3) – COOH 4) – CHO
8. Which of the following shows structure of allylic alcohol?
   (i) CH_2 =CH -CH_2OH (ii) CH_2 =CH –OH
   (iii) CH_2=CH-CH(CH_3)OH (iv) CH_2 = CH - C (CH_3)$_2$ OH
   1) (i), (iii) and (iv) 2) (i), (ii) and (iv) 3) (ii), (iii) and (iv) 4) (i), (ii), (iii) and (iv)

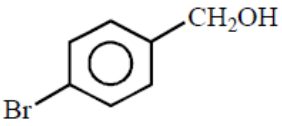
TOPIC 2: Preparation and Properties of Alcohols

9. Consider the following alcohols,

(I) 

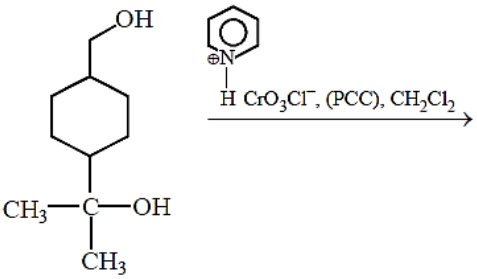
(III) 

(II) 

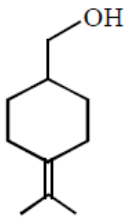
(IV) 

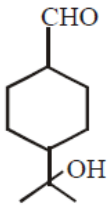
The order of decreasing reactivities of these alcohols towards nucleophilic substitution with HBr is:

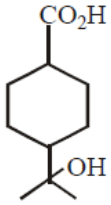
1) III > I > IV > II 2) III > I > II > IV 3) I > III > IV > II 4) I > III > II > IV

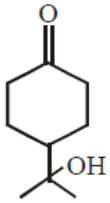
10. 

Product of the reaction is:

(a) 

(b) 

(c) 

(d) 

11. Which are not cleaved by HIO_4?

I. glycerol II. Glycol III. 1, 3 propenediol IV. methoxy-2-propanol

1) I, II, III, IV 2) I, II 3) II, III 4) III, IV

12. Which of the esters shown, after reduction with $LiAlH_4$ and aqueous workup, will yield two molecules of only a single alcohol?

1) $CH_3CH_2CO_2CH_2CH_3$ 2) $C_6H_5CO_2CH_2C_6H_5$

3) $C_6H_5CO_2C_6H_5$ 4) None of these

13. For the following reaction, select the statement that best describes the change

$$RCH_2OH + PCC\left[C_5H_5NH^+ClCrO_3^-\right] \rightarrow$$

1) The alcohol is oxidized to an acid, and the Cr(VI) is reduced.
2) The alcohol is oxidized to an aldehyde, and the Cr(VI) is reduced.
3) The alcohol is reduced to an aldehyde, and the Cr(III) is oxidized.
4) The alcohol is oxidized to a ketone, and the Cr(VI) is reduced.

14. Ethyl alcohol is industrially prepared from ethylene by

1) Permanganate oxidation 2) Catalytic reduction

3) Absorbing in H_2SO_4 followed by hydrolysis 4) All the three

15. Iodoform can be obtained on warming NaOH and iodine with:

(a) $CH_3CH_2CH(OH)CH_3$

(b) $(CH_3)_2CHCC_2H_5$ (O)

(c) $CH_3-C(=O)-OCH_3$

(d) $(CH_3)_2CHCH_2OH$

16. $C_6H_5-CH=CHCHO \xrightarrow{X} C_6H_5CH=CHCH_2OH$ In the above sequence, X can be

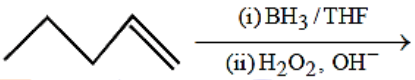
1) N_2 / Ni 2) $NaBH_4$ 3) $K_2Cr_2O_7$ / H+ 4) Both 1) and 2)

17. Formation of which compound given below from 1 - butanol needs an oxidising agent?

1) $CH_3CH_2CH_2CH_2Br$ 2) $CH_3CH_2CH_2CH=O$

3) $(CH_3CH_2CH_2CH_2)_2O$ 4) $CH_3\text{-}CH_2CH=CH_2$

18. The product of the following reaction is



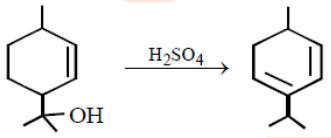
1) 1-Pentanol 2) 2-Pentanol 3) Pentane 4) 1,2-Pentanediol

19. $CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$

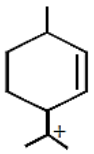
In the above reaction, the leaving group is

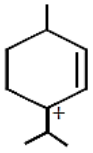
(a) OH^- (b) H_2O

(c) $HO-\overline{Z}nCl_2$ (d) H_3O^+

20. 

Which carbocation is involved in the above reaction ?

(a) 

(b) 

(c) Both (d) None

21. Rate of dehydration of alcohols follows the order:

1) 2° > 1° > CH_3OH > 3° 2) 3° > 2° > 1° > CH_3OH

3) 2° > 3° > 1° > CH_3OH 4) CH_3OH > 1° > 2° > 3°

22. Reagent used to convert allyl alcohol to acrolein is

1) MnO_2 2) H_2O_2 3) OsO_4 4) $KMnO_4$

23. HBr reacts fastest with

1) 2-Methylpropan-1-ol 2) 2-Methylpropan-2-ol 3) propan-2-ol 4) propan-1-ol.

24. The best method to prepare cyclohexene from cyclohexanol is by using

1) Conc. HCl + $ZnCl_2$ 2) Conc. H_3PO_4 3) HBr 4) Conc. HCl

25. Acid catalyzed hydration of alkenes except ethene leads to the formation of
1) primary alcohol 2) secondary or tertiary alcohol
3) mixture of primary and secondary alcohols 4) mixture of secondary and tertiary alcohols

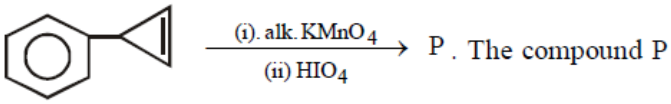
26. Which of the following reagent is best to change glycerol to acrolein ?
1) P_2O_5 2) Conc. H_2SO_4 3) Anhydrous $CaCl_2$ 4) $KHSO_4$

27. Which one of the following alcohols is least soluble in water?
1) CH_3OH 2) C_3H_7OH 3) C_4H_9OH 4) $C_{10}H_{21}OH$

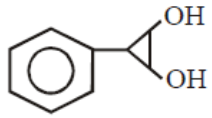
28. Which of the following will not give iodoform test?
1) Isopropyl alcohol 2) Ethanol 3) Ethanal 4) Benzyl alcohol

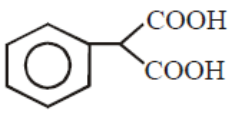
29. Ethyl alcohol can be prepared from Grignard reagent by the reaction of :
1) HCHO 2) R_2CO 3) RCN 4) RCOCl

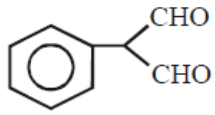
30. Glycerol is more viscous than ethanol due to
1) high molecular weight 2) high boiling point
3) many hydrogen bonds per molecule 4) Fajan's rule

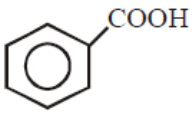
31. 

P. The compound P should be

(a) 

(b) 

(c) 

(d) 

32. When glycerol is treated with excess of HI, it produces
1) Glycerol triiodide 2) 2–iodopropane 3) allyl iodide 4) propene

33. Which of the following compounds can be used as antifreeze in automobile radiators?
1) Methyl alcohol 2) Glycol 3) Nitro phenol 4) Ethyl alcohol

34. In the following sequence of reactions
$CH_3 - Br \xrightarrow{KCN} A \xrightarrow{H_3O^+}$
$B \xrightarrow[ether]{LiAlH_4} C$, the end product (C) is :
1) Acetone 2) Methane 3) Acetaldehyde 4) Ethyl alcohol

35. Number of isomeric alcohols of molecular formula C6H14O which give positive iodoform test is
1) two 2) three 3) four 4) five

36. Which of the following reaction (s) can be used for the preparation of alkyl halides ?
(I) $CH_3CH_2OH + HCl \xrightarrow{anhy.ZnCl_2}$
(II) $CH_3CH_2OH + HCl \longrightarrow$
(III) $(CH_3)_3COH + HCl \longrightarrow$
(IV) $(CH_3)_2CHOH + HCl \xrightarrow{anhy.ZnCl_2}$
1) (I), (III) and (IV) only 2) (I) and (II) only 3) (IV) only 4) (III) and (IV) only

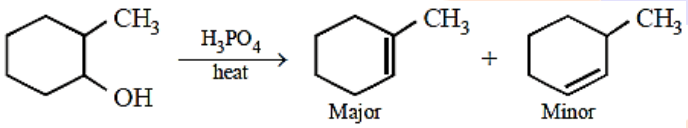
37. Isopropyl alcohol is obtained by reacting which of the following alkenes with concentrated H2SO4 followed by boiling with H_2O?
1) Ethylene 2) Propylene 3) 2-Methylpropene 4) Isoprene

38. Commercially carboxylic acids are reduced to alcohols by converting them to the _____.

1) esters 2) aldehydes 3) ketones 4) amines

39. Alcohols of low molecular weight are
1) soluble in water 2) soluble in water on heating
3) insoluble in water 4) insoluble in all solvents

40. When ethyl alcohol reacts with acetic acid, the products formed are
1) Sodium ethoxide + hydrogen 2) Ethyl acetate + water
3) Ethyl acetate + soap 4) Ethyl alcohol + water

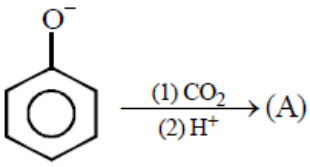
41. 

The above reaction is in example of
1) regiospecific 2) regioselective 3) stereoselective 4) stereospecific

42. Methanol and ethanol can be distinguished by the following:
1) By reaction with metallic sodium 2) By reaction with caustic soda
3) By heating with iodine and washing soda 4) By heating with zinc and inorganic mineral acid

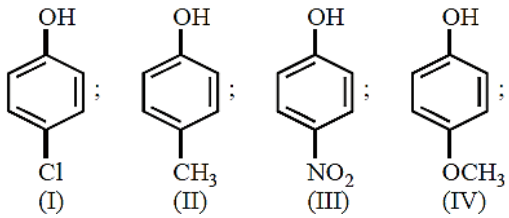
43. The compound which reacts fastest with Lucas reagent at room temperature is
1) Butan-1-ol 2) Butan-2-ol 3) 2-Methyl propan-1-ol 4) 2-Methylpropan-2-ol

44. Which of the following compounds will react with sodium hydroxide solution in water?
1) C_6H_5OH 2) $C_6H_5CH_2OH$ 3) $(CH_3)_3COH$ 4) C_2H_5OH

45. 

Which of the following is true statement about the reaction?
1) Ortho isomer is major if PhONa is used 2) Para isomer is major if PhOK is used
3) Product formed is further used for preparation of drug aspirin
4) All of these

46. The major reason that phenol is a better Bronsted acid than cyclohexanol is that
1) it is a beter proton donor.
2) the cyclohexyl group is an electron donating group by induction, which destabilizes the anion formed in the reaction by resonance.
3) phenol is able to stabilize the anion formed in the reaction.
4) the phenyl group is an electron withdrawing group by induction, which stabilizes the anion formed in the reaction.

47. Arrange the following compounds in order of decreasing acidity :


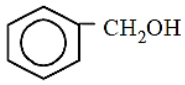
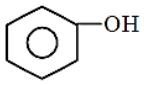
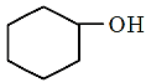
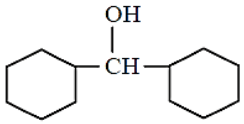
1) II > IV > I > III 2) I > II > III > IV 3) III > I > II > IV 4) IV > III > I > II

48. Which one of the following compounds will be most readily attacked by an electrophile?
1) Chlorobenzene 2) Benzene 3) Phenol 4) Toluene

49. Phenol is less acidic than
1) acetic acid 2) *p*-methoxyphenol 3) acetylene 4) ethanol

50. To distinguish between salicylic acid and phenol, one can use :
1) $NaHCO_3$ solution 2) 5% NaOH solution 3) neutral $FeCl_3$ 4) bromine water

51. Which one of the following compounds has the most acidic nature?

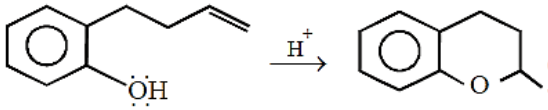
(a) 
(b) 
(c) 
(d) 

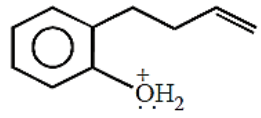
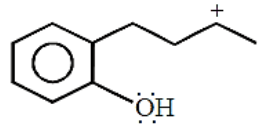
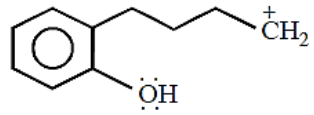
52. Among the following four compounds
(i) phenol (ii) methylphenol (iii) *meta*-nitrophenol (iv) *para*-nitrophenol
the acidity order is :
1) ii > i > iii > iv 2) iv > iii > i > ii 3) iii > iv > i > ii 4) i > iv > iii > ii

53. Which of the following is not true in case of reaction with heated copper at 300°C?
1) Phenol → Benzyl alcohol 2) Secondary alcohol → Ketone
3) Primary alcohol → Aldehyde 4) Tertiary alcohol → Olefin

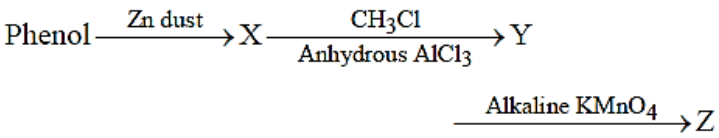
54. Arrange the following in increasing order of their acidity?
o–cresol1), salicylic acid2), phenol3)
1) c < a < b 2) b < c < a 3) a < b < a 4) a < c < b

55. Which of the following ion is formed in the following reaction?



(a) 
(b) 
(c) 
(d) All the three

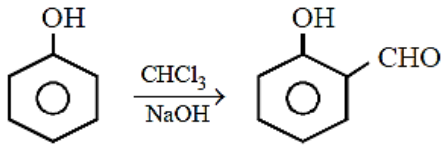
56. Consider the following reaction:



The product Z is
1) benzaldehyde 2) benzoic acid 3) benzene 4) toluene

57. Given are cyclohexanol (I), acetic acid (II), 2, 4, 6 – trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be :
1) III > II > IV > I 2) II > III > I > IV 3) II > III > IV > I 4) III > IV > II > I

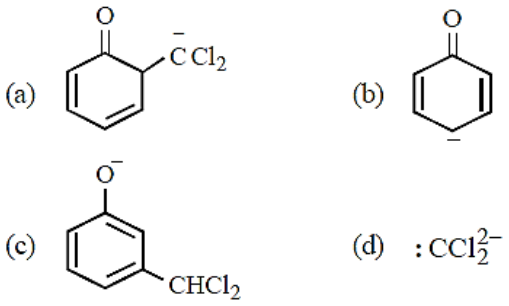
58. Which electrphile is likely to be formed as an intermediate in the following electrophilic substitution reaction ?



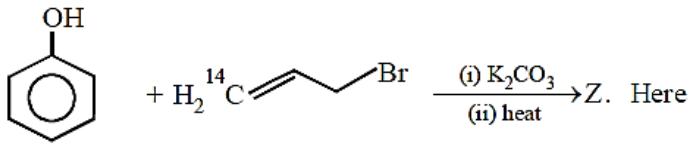
(a) $\overset{+}{C}HCl_2$ (b) $\overset{+}{C}HO$

(c) $:\overset{+}{C}Cl_2$ (d) $:CCl_2$

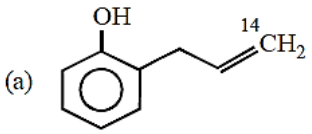
59. Which of the following is not formed as an intermediate in the Reimer- Tiemann reaction between phenol and alkaline chloroform ?

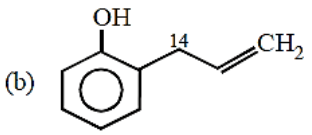


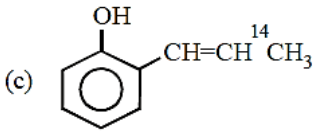
60.

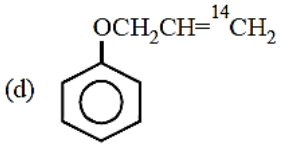


Z is

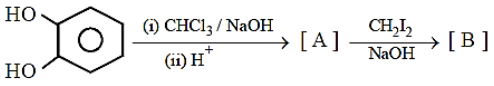


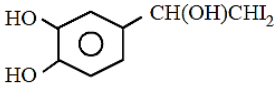


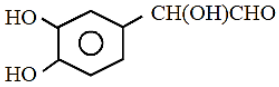


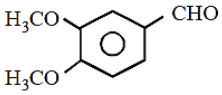


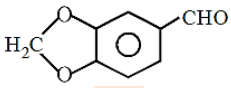
61. Identify the product [B] in the following reaction

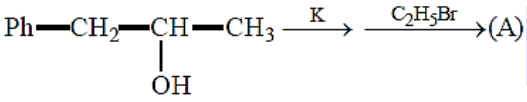


(a) 

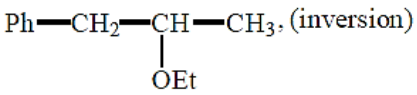
(b) 

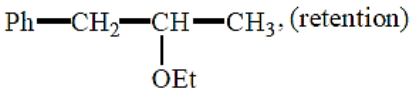
(c) 

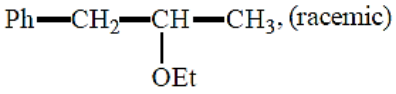
(d) 

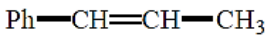
62. 

Product (A) in above reaction is:

(a) 

(b) 

(c) 

(d) 

63. Which yields isopropyl methyl ether with little or no by products ?

(a) $(CH_3)_2CHO^-Na^+ + CH_3I \longrightarrow$

(b) $CH_3O^-Na^+ + (CH_3)_2CHI \longrightarrow$

(c) $(CH_3)_2CHOH + CH_3OH \xrightarrow{H_2SO_4}$

(d) All of these

64. Which of the following cannot be made by using Williamson's synthesis?

1) Methoxybenzene 2) Benzyl *p*-nitrophenyl ether

3) Methyl tertiary butyl ether 4) Di-tert-butyl ether

65. *tert*-Butyl ethyl ether can't be prepared by which reaction?

1) *tert* Butanol+ ethanol $\xrightarrow{H^+}$ 2) *tert*-Butyl bromide + sodium ethoxide $\longrightarrow$

3) Sodium *tert*-butoxide + ethyl bromide $\longrightarrow$ 4) Isobutene + ethanol $\xrightarrow{H^+}$

66. Which one is formed when sodium phenoxide is heated with ethyl iodide ?

1) Phenetole 2) Ethyl phenyl alcohol 3) Phenol 4) None of these

67. In Williamson's synthesis, ethoxyethane is prepared by

1) passing ethanol over heated alumina 2) sodium ethoxide with ethyl bromide

3) ethyl alcohol with sulphuric acid 4) ethyl iodide and dry silver oxide

68. Which of the following compound is soluble in ether?

1) Oils & fats 2) Water 3) NaCl 4) PCl5

69. The reaction of sodium ethoxide with ethyl iodide to form diethyl ether is termed

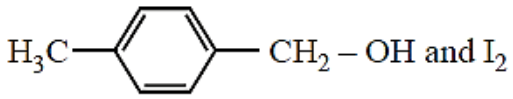
1) electrophilic substitution 2) nucleophilic substitution
3) electrophilic addition 4) radical substitution

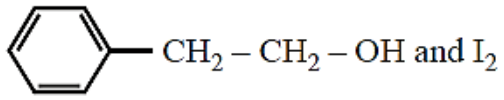
70. Which of the following product is formed, when ether is exposed to air ?
1) Oxide 2) Alkanes 3) Alkenes 4) Peroxide of diethyl ether

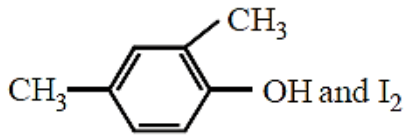
NEET PREVIOUS YEARS QUESTIONS

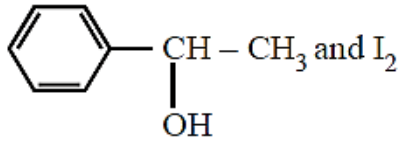
1. The compound A on treatment with Na gives B and with PCl_5 gives C. B and C react together to give diethyl ether. A, B and C are in the order. **[2018]**
1) C_2H_5OH, C_2H_6, C_2H_5Cl 2) C_2H_5OH, C_2H_5Cl, C_2H_5ONa
3) C_2H_5 OH, C_2H_5ONa, C_2H_5Cl 4) C_2H_5Cl, C_2H_6, C_2H_5OH

2. 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 **[2018]**

(a) 

(b) 

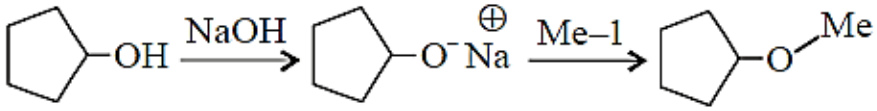
(c) 

(d) 

3. The heating of phenyl-methyl ethers with HI produces **[2017]**
1) iodobenzene 2) phenol 3) benzene 4) ethyl chlorides

4. Which of the following reagents would distinguish cis-cyclopenta-1,2-diol from the trans-isomer? **[2016]**
1) Acetone 2) Ozone 3) MnO_2 4) Aluminium isopropxide

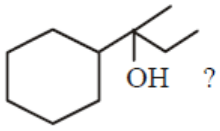
5. The reaction

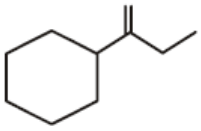


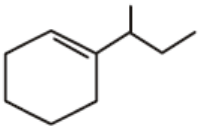
can be classified as :- **[2016]**
1) Williamson ether synthesis reaction 2) Alcohol formation reaction
3) Dehydration reaction 4) Williamson alcohol synthesis reaction

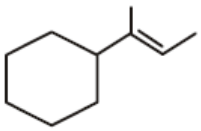
6. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group? **[2015]**
1) $–CH_2Cl$ 2) –COOH 3) $–CHCl_2$ 4) –CHO

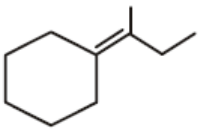
7. Which of the following is not the product of dehydration of **[2015]**



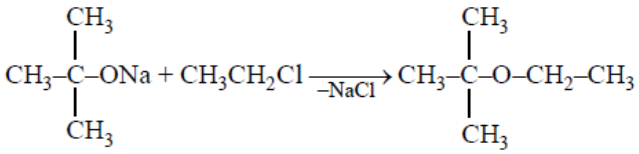
(a) 

(b) 

(c) 

(d) 

8. The reaction



is called **[2015]**

a) Williamson continuous etherification process
2) Etard reaction
3) Gatterman - Koch reaction
4) Williamson Synthesis

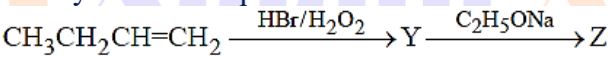
9. Among the following sets of reactants which one produces anisole? **[2014]**

1) CH_3CHO; RMgX
2) C_6H_5OH; NaOH ; CH_3I
3) C_6H_5OH; neutral $FeCl_3$
4) C_6H_5–CH_3; CH_3COCl; $AlCl_3$

10. Which of the following will not be soluble in sodium hydrogen carbonate? **[2014]**

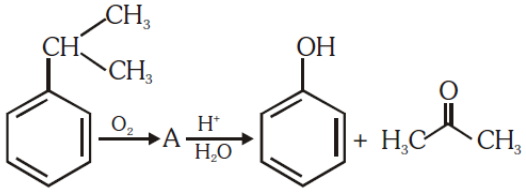
1) 2, 4, 6-trinitrophenol
2) Benzoic acid
3) *o*-Nitrophenol
4) Benzenesulphonic acid

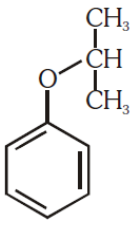
11. Identify Z in the sequence of reactions: **[2014]**

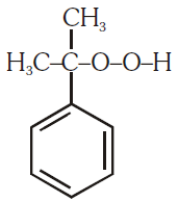


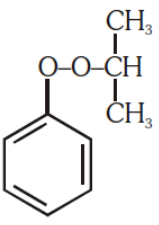
(a) CH_3—$(CH_2)_3$—O—CH_2CH_3
(b) $(CH_3)_2CH_2$—O—CH_2CH_3
(c) $CH_3(CH_2)_4$—O—CH_3
(d) CH_3CH_2—$CH(CH_3)$—O—CH_2CH_3

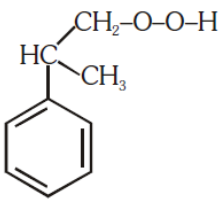
12. The structure of intermediate A in the following reaction is:- **[2019]**



(1) 

(2) 

(3) 

(4) 

13. When vapours of a secondary alcohol is passed over heated copper at 573 K, the product formed is :- **[2019 –ODISSA]**

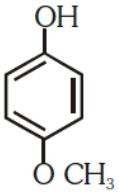
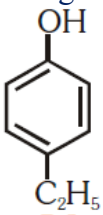
(1) a carboxylic acid
(2) an aldehyde
(3) a ketone
(4) an alkene

14. The major products C and D formed in the following reactions respectively are :- **[2019 –ODISSA]**

$H_3C–CH_2–CH_2–O–C(CH_3)_3 \xrightarrow[\Delta]{\text{excess HI}} C + D$

(1) $H_3C–CH_2–CH_2–I$ and $I–C(CH_3)_3$ (2) $H3C–CH_2–CH_2–OH$ and $I–C(CH_3)_3$
(3) $H_3C–CH_2–CH_2–I$ and $HO–C(CH_3)_3$ (4) $H_3C–CH_2–CH_2–OH$ and $HO–C(CH_3)_3$

15. Which of the following substituted phenols is the strongest acid? **[2020-COVID]**

(1)  (2)  (3)  (4) 

16. $CH_3CH_2CH=CH_2 \xrightarrow[H_2O,H_2O_2,OH^-]{B_2H_6} Z$ What is Z? **[2020-COVID]**

(1) $CH_3CH_2CH_2CH_2OH$ (2) $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$
(3) $CH_3CH_2CH_2CHO$ (4) $CH_3CH_2CH_2CH_3$

17. Reaction between acetone and methylmagnesium chloride followed by hydrolysis will give: **[2020]**

1. Isobuty alcohol 2. Isopropyl alcohol
3. Sec butyl alcohol 4. Tert butyl alcohol

18. What is the IUPAC name of the organic compound formed in the following chemical reaction?

$\text{Acetone} \xrightarrow[(ii)H_2O,H^+]{(i)C_2H_5MgBr,\,dry\,Ether} \text{Product}$ **[NEET-2021]**

1) Pentan-2ol 2) Pentan-3-ol
3) 2-methyl butan-2-ol 4) 2-methyl propan-2-ol

19. Given below are two statements **[NEET-2022]**

Statement I : The acidic strength of monosubstitued nitrophenol is higher than phenol because of electron withdrawing nitro group.

Statement II :o-nitrophenol, m- nitrophenol and p-nitrophenol will have same acidic strength as they have one nitro group attached to the phenolic ring.

In the light of the above statements, choose the most appropriate answer from the options given below:

1) Both statement I and Statement II are correct
2) Both statement I and Statements II are incorrect
3) Statement I is correct but Statement II is incorrect
4) Statement I is incorrect but statement II is correct

20. Given below are two statements: **[NEET-2022]**

Statement I: In Lucas test, primary, secondary and tertiary alcohols are distinguished on the basis of their reactivity with conc, $HCl+ZnCl_2$, known as Lucas Reagent

Statements II: Primary alcohols are most reactive and immediately produce turbidity at room temperature on reaction with Lucas Reagent

In the light of the above statements, choose the most appropriate answer from the options given below:

1) Both Statement I and Statements II are correct
2) Both Statements I and Statements II are incorrect
3) Statement I is correct but Statement II is Incorrect
4) Statement I is incorrect but Statement II is correct

NCERT LINE BY LINE QUESTIONS – ANSWERS

(1.)	b	**(2.)**	a	**(3.)**	d	**(4.)**	c	**(5.)**	c
(6.)	d	**(7.)**	c	**(8.)**	c	**(9.)**	b	**(10.)**	b
(11.)	b	**(12.)**	c	**(13.)**	c	**(14.)**	b	**(15.)**	b
(16.)	d	**(17.)**	a	**(18.)**	c	**(19.)**	c	**(20.)**	a
(21.)	a	**(22.)**	a	**(23.)**	c	**(24.)**	c	**(25.)**	c
(26.)	c	**(27.)**	d	**(28.)**	d	**(29.)**	c	**(30.)**	c
(31.)	a	**(32.)**	c	**(33.)**	d	**(34.)**	c	**(35.)**	b
(36.)	c	**(37.)**	b	**(38.)**	d	**(39.)**	b	**(40.)**	c
(41.)	d	**(42.)**	c	**(43.)**	b	**(44.)**	b	**(45.)**	c
(46.)	c	**(47.)**	a	**(48.)**	b	**(49.)**	b	**(50.)**	a

TOPIC WISE PRACTICE QUESTIONS - ANSWERS

1) 2	**2)** 2	**3)** 3	**4)** 3	**5)** 2	**6)** 2	**7)** 2	**8)** 1	**9)** 1	**10)** 2
11) 4	**12)** 2	**13)** 2	**14)** 3	**15)** 1	**16)** 2	**17)** 2	**18)** 1	**19)** 3	**20)** 3
21) 2	**22)** 1	**23)** 2	**24)** 2	**25)** 2	**26)** 4	**27)** 4	**28)** 4	**29)** 1	**30)** 3
31) 3	**32)** 2	**33)** 2	**34)** 4	**35)** 3	**36)** 1	**37)** 2	**38)** 1	**39)** 1	**40)** 2
41) 2	**42)** 3	**43)** 4	**44)** 1	**45)** 4	**46)** 4	**47)** 3	**48)** 3	**49)** 1	**50)** 1
51) 2	**52)** 2	**53)** 1	**54)** 4	**55)** 2	**56)** 2	**57)** 1	**58)** 4	**59)** 4	**60)** 2
61) 4	**62)** 2	**63)** 1	**64)** 4	**65)** 2	**66)** 1	**67)** 2	**68)** 1	**69)** 2	**70)** 4

NEET PREVIOUS YEARS QUESTIONS-ANSWERS

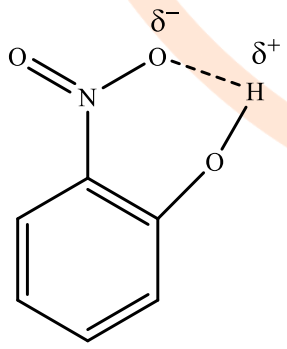
1) 3	**2)** 4	**3)** 2	**4)** 1	**5)** 1	**6)** 4	**7)** 2	**8)** 4	**9)** 2	**10)** 3
11) 1	**12)** 2	**13)** 3	**14)** 1	**15)** 1	**16)** 1	**17)** 4	**18)** 3	**19)** 3	**20)** 3

NCERT LINE BY LINE QUESTIONS – SOLUTIONS

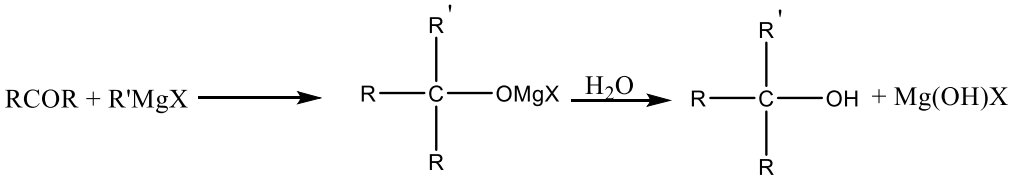
(1.) **(b.)** Depending upon whether the alkyl halide and alkoxide ion carry the same or different alkyl groups, both symmetrical and unsymmetrical ethers can be prepared by Williamson's synthesis.

(2.) **(a.)** Both A and R are correct and R is the correct explanation of A.

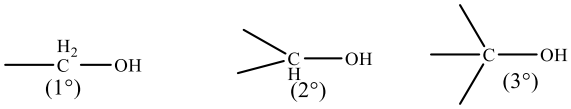
(3.) (d) o-nitrophenol is steam volatile due to intramolecular H-bonding.



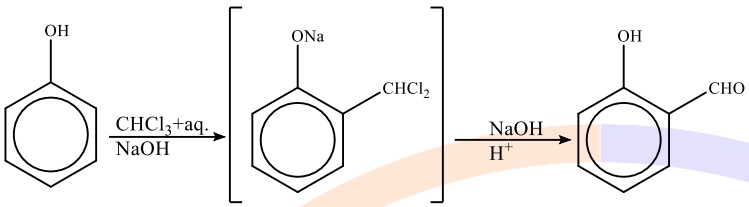
(4.) (c) Complete reaction is as follows



(5.) (c) Option c is the tertiary alcohol. The three type of alcohols, the OH group is attached to primary, secondary and tertiary carbon atom

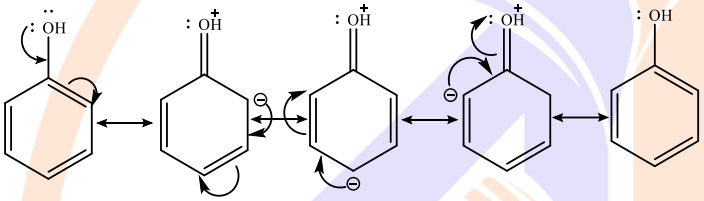


(6.) (d) Reaction of phenol with chloroform in the presence of dilute sodium hydroxide finally introduces –CHO functional group. This reaction is called Reimer–Tiemann reaction

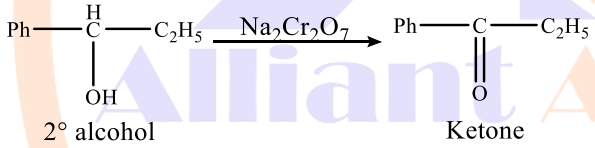


(7.) (c) Steps involved in the acid catalysed hydration are as follows:
(I) Protonation of alkene to form carbocation by electrophilic attack of H_3O+
(II) Nucleophilic attack of water or carbocation
(III) Deprotonation to form an alcohol

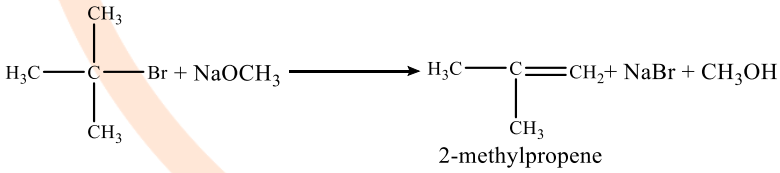
(8.) (c) The resonating structures of phenol are as follows



(9.) **(b.)** Degree of unsaturation in A is benzene ring. Degree of unsaturation in B is (benzene ring and 1 >C O group. Hence, 'A' is 2° alcohol.

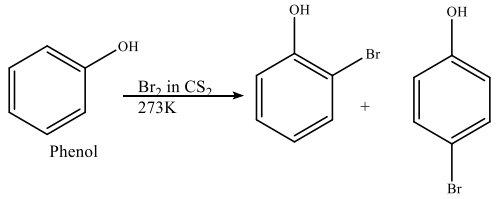


(10.) **(b.)** If a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.



(11.) **(b.)** Only statement **(b)** is correct. Other statements are incorrect and corrected as:
- The simplest hydroxy benzene is phenol.
- Dihydroxy derivatives of benzene are known as 1,2-, 1,3- and 1,4-benzenediol.
- The word ether is used in case of IUPAC name ether.

(12.) (c) Alcohols are versatile compound. They react both as electrophile and nucleophiles.



(13.) (c)

(14.) **(b.)** In sunlight, monochlorination of toluene gives benzyl chloride. On hydrolysis with aq. NaOH, benzyl chloride shows nucleophilic reaction to give benzyl alcohol.

(15.) **(b.)** During esterification when the size of the alkyl group in either acid or alcohol increases, the rate of esterification decreases. Since, there is steric hindrance in $(CH_3)_3COH$ than in CH_3OH, it undergoes esterification slower than CH_3OH.

(16.) (d) Williamson synthesis involves nucleophilic substitution reaction. It is not an electrophilic substitution reaction.

(17.) **(a.)** Vinylic alcohols contain $-OH$ group bonded to a $C-C$ double bond i.e. to a vinylic carbon or to an aryl carbon. These alcohols are also known as vinylic alcohols $CH_2=CH-OH$

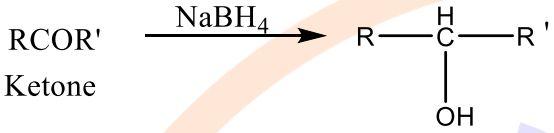
(18.) (c) Methanol, CH_3OH, also known as wood spirit.

(19.) (c) In phenol, high electronegatively of sp^2 hydridised carbon to which –OH is attached.

(20.) **(a.)** In vinylic phenol, the –OH group is attached directly to $C=C$, i.e. $-C=C-OH$. So, the correct structure is **(a)**.

(21.) **(a.)** The given reaction is called Williamson synthesis. The reaction involves the formation of ether on reaction of Na salt with alkyl halide in presence of dry ether

(22.) **(a.)** Product 'Y' is 2° alcohol. Complete reaction is



2° alcohol

(23.) (c) Ordinary spirit used for polishing wooden furniture contain hydroxyl group, ethanol.

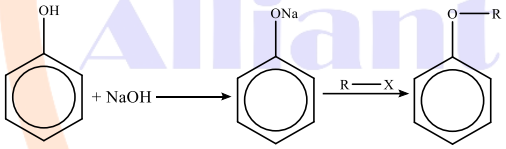
(24.) (c) The carbon oxygen bond length in phenol is slightly less than that in methanol. This is due to

(i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and

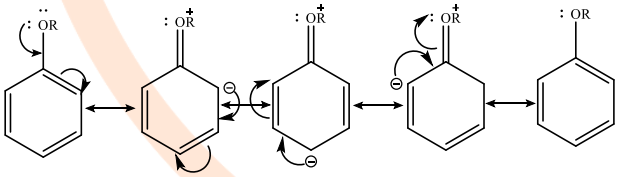
(ii) sp2 hydridised state of carbon to which oxygen is attached.

(25.) (c) An electron releasing group $(-C_2H_5)$ increases electron density on oxygen tending to decrease the polarity of $O-H$ bond. This decreases the acidic strength.

(26.) (c) The reagents used to carry out the conversion is NaOH, R–X.



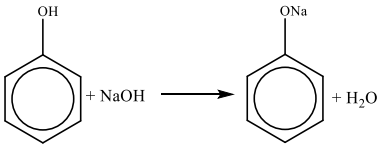
(27.) (d) The incorrect structure is (d). Resonating structures are as follows:



(28.) (d) Statement (d) is wrong.

(29.) (c) The difference in reactivity of three classes of alcohols with HCl distinguishes them from one another.

(30.) (c) Reaction (c) is correct



The given reaction show that alcohols and phenols are acidic in nature.

(31.) **(a.)** Both **(A)** and (R) are correct and also R is the correct explanation of A.

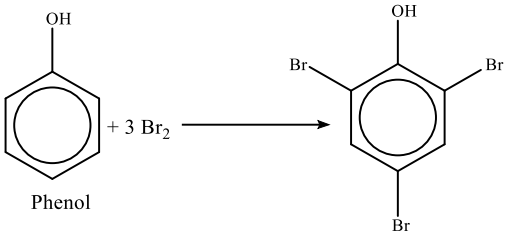
(32.) (c) A mixture of conc. HCl and anhyd. ZnH_2 is called Lucas reagent.

(33.) (d) $(CH_3)_3CO^-N^+a$ and CH_3CH_2Br react to form $(CH_3)_3C-O-CH_2CH_3$. Good yields of ethers are obtained when primary alkyl halides are treated with alkoxides derived from any alcohol 1°, 2° or 3°

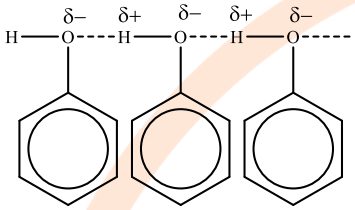
(34.) (c) The bond angle $C-O-H$ in alcohols is slightly less than the tetrahedral angle 109°28. It is due to the repulsion between is shared pairs of oxygen. Thus, A is correct but R is incorrect.

(35.) **(b.)** I → r, II → q, III → p

(36.) (c) When phenol is treated with bromine water, 2,4,6-tribromophenol is formed as white precipitate.

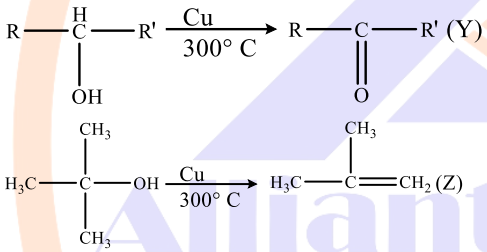


(37.) **(b.)** The –OH group in alcohols and phenols is involved in intermolecular H-bonding as shown below:



(38.) (d) Since oxidation is easier and occurs very quickly (just 2 sec), hence it must be a primary alcohol. The dichromate solution changes from orange to blue green.

(39.) **(b)** $RCH_2OH \xrightarrow[573K]{Cu} R-CHO\ (X)$



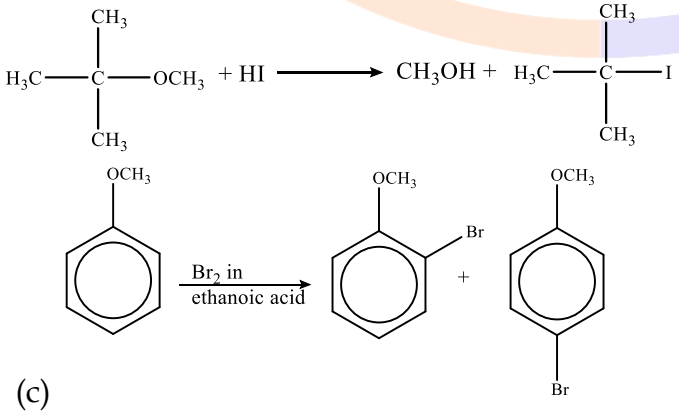
(40.) (c) The correct structure of phenyl isopentyl ether, $C_6H_5OCH_2CH_2CH(CH_3)CH_3$ IUPAC name is 3-methylbutoxy benzene

(41.) (d) Branching in organic molecules give rise to a decrease in surface area and thus, intermolecular forces among the molecules decease to show low boiling points. The difference between boiling points of two consecutive members of alcohols is about 18–20 K.

(42.) (c) The correct increasing order of boiling point is IV < III < II < I. Boiling point increases with increase in the number of carbon atoms.

(43.) **(b.)** Steps involved in the reaction are Step I: Formation of protonated alcohol. Step II: Formation of carbocation. Step III: Formation of ethene by elimination of a proton.

(44.) **(b.)** When one of the alkyl group is a tertiary group, the halide formed is a tertiary halide



(45.) (c)

(46.) (c) The given compound A is $C_4H_{10}O$. All the reactions are as follows:

$CH_3CH_2OCH_2CH_3 \xrightarrow{conc.\ H_2SO_4} [CH_3CH_2OHCH_2CH_3]$

soluble oxonium salt

$$CH_3CH_2OCH_2CH_3 \xrightarrow[(Excess),\Delta]{HI} 2CH_3CH_2I + H_2O$$

Diethyl ether (A)

(47.) **(a.)** The order of reactivity of hydrogen halides with ether is HI > HBr > HCl

(48.) **(b.)** Invertase enzyme is used to hydrolyse sucrose ($C_{12}H_{22}O_{11}$).

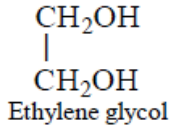
$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

(49.) **(b.)** On treating phenol with $CHCl_3$ in the presence of NaOH, a -CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer–Tiemann reaction.

(50.) **(a.)** The correct boiling point order and solubility order is II > III > I. In II, three OH groups are present. Hence, more H-bonding in II. In III, only one OH is present. Hence, less H-bonding is present. In alkane (I), Van der Waals interaction are present.

TOPIC WISE PRACTICE QUESTIONS - SOLUTIONS

1. 2) Glycols are dihydric alcohols (having two hydroxyl groups). Ethylene glycol is the first member of this series.



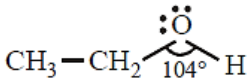
Ethylene glycol

2. 2)

3. 3)Ethers contain the functional group – O –

4. (3) Alcoholic beverages contain ethyl alcohol (C_2H_5OH) which is drinking alcohol. CH_3OH is poisonous alcohol.

5. (2) In C_2H_5OH,



Due to presence of lone pair of electrons on oxygen, there occurs a small decrease in bond angle from the normal tetrahedral bond angle (109°28').

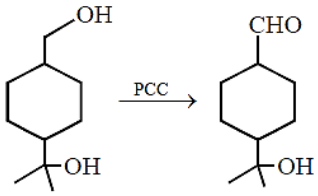
6. (2) $CH_3CH_2CH(OH)CH_3$ is a secondary alcohol

7. (2) Cresol has phenolic group – OH

8. (1) $CH_2 = CH$ -OH represents vinylic alcohol. In vinylic alcohols, –OH group is attached to sp^2 hybridized carbon whereas in allylic alcohols, – OH group is attached to sp^3 hybridized carbon.

9. (1) More stable carbocation more is the rate toward HBr (acid)

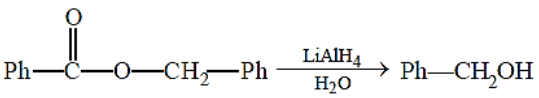
10. 2)



(3° alcohol cannot be oxidized)

11. 4) HIO_4 will not oxidise, diol from 1, 3 atom and not used for cleavage of ether.

12. 2)



(2 mole)

13. 2) $Cr^{6+} \rightarrow Cr^{3+}$ (PCC oxidises 1° alcohol to aldehyde)

14. (3) Ethylene is passed into concentrated sulphuric acid at 75–80°C under pressure when a mixture of ethyl hydrogen sulphate is formed. Which on heating ethyl alcohol.

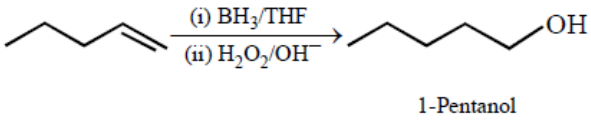
$$\underset{\text{Ethylene}}{H_2C=CH_2}+H_2SO_4 \xrightarrow{100^\circ C} C_2H_5HSO_4$$

$$\xrightarrow[H_2O]{\Delta} C_2H_5OH + H_2SO_4$$

15. 1) 2-Butanol.
16. (2) $NaBH_4$ and $LiAlH_4$ attack only carbonyl group and reduce it into alcohol group.

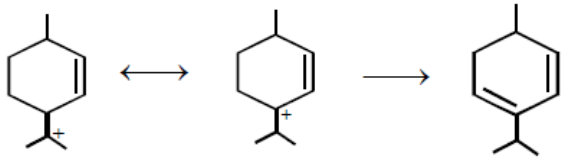
$$\underset{\text{Cinnamic aldehyde}}{C_6H_5-CH=CHCHO} \xrightarrow{NaBH_4} \underset{\text{Cinnamyl alcohol}}{C_6H_5-CH=CHCH_2OH}$$

17. 2) $CH_3CH_2CH_2CH_2OH \xrightarrow{\text{Oxidation}} CH_3CH_2CH_2CHO$
18. 1) Hydroboration-oxidation leads to *anti*-Markownikoff's hydration, thus



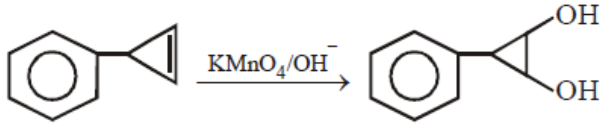
1-Pentanol

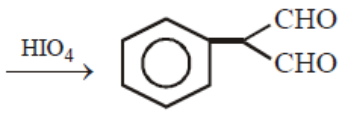
19. (3) Zinc chloride is a Lewis acid and coordinates with the alcoholic group
20. 3)



3° 3° allylic (more stable)

21. (2) The order of dehydration among three type of alcohols is 3° > 2° > 1° > CH_3OH. This behaviour is related to the relative stabilities of carbocations (3° > 2° > 1°).
22. (1) MnO_2 being a mild oxidising agent stops the oxidation of – CH_2OH group at aldehyde stage.
23. (2) Greater the stability of the intermediate carbocation, more reactive is the alcohol. Since 2-methylpropan-2-ol generates 3° carbocation, therefore, it reacts fastest with HBr.
24. (2) Conc. HCl, HBr and conc. HCl + $ZnCl_2$ all are nucleophiles, thus convert alcohols to alkyl halides. However, conc. H_3PO_4 is a good dehydrating agent which converts an alcohol to an alkene.
25. 2)
26. 4) Glycerol is dehydrated by using dehydrating agent like P_2O_5 or conc H_2SO_4 or $KHSO_4$ but $KHSO_4$ is best of them.
27. 4) Solubility of alcohol in water decreases with increase in molecular mass due to increase in water repelling alkyl part in alcohol.
28. 4) $C_6H_5CH_2OH$ does not give iodoform test because it has neither CH_3CO— group nor CH_3CHOH |R group.
29. 1)
30. 3) Because of larger number of intermolecular hydrogen bonding (three per molecule) in case of glycerol ($CH_2OH - CHOH - CH_2OH$) as compared to ethanol (CH_3CH_2OH), the attraction between molecules of glycerol is more than that between molecules of ethanol. Due to this glycerol is more viscous than ethanol.
31. 3)





32. (2) Glycerol when treated with excess HI produces 2–iodopropane
33. (2) Glycol is used as an antifreeze in automobiles.

34. 4)

$$CH_3-Br \xrightarrow{KCN} \underset{(A)}{CH_3-CN} \xrightarrow{H_3O^+}$$

$$\underset{(B)}{CH_3-COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethyl alcohol}}{\underset{(C)}{CH_3-CH_2-OH}}$$

35. 3) Compound containing $CH_3CH(OH)$ or CH_3CO–group give positive iodo form test.

36. (1) $ZnCl_2$ is a lewis acid and interact with alcohol. Carbocation is formed as intermediate in the SN 1 mechanism which these reaction undergoes. In the absence of $ZnCl_2$ formation of primary carbocation is difficult which is the case with (ii) while (i) undergoes reaction. (iii) Tertiary carbocation casily formed due to the stability. (iv) In the presence of $ZnCl_2$, 2° carbocation is formed

from $(CH_3)_2-\underset{\displaystyle H}{\underset{|}{C}}-OH$ i.e., $CH_3-\overset{\oplus}{C}H-CH_3$

37. 2) Since the compound is formed by hydration of an alkene, to get the structure of alkene remove a molecule of water from the alcohol.

$$\underset{\displaystyle OH}{\underset{|}{CH_3CHCH_3}} \xrightarrow{-H_2O} CH_2=CHCH_3$$

Isopropyl alcohol — Propylene

38. (1) Commercially, acids are reduced to alcohols by converting them to the esters, followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

$$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[\text{Catalyst}]{H_2} RCH_2OH + R'OH$$

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

40. 2) $C_2H_5OH + CH_3COOH \longrightarrow CH_3COOC_2H_5 + H_2O$

41. (2) Reactions where one of the products is major are known as regioselective.

42. (3) Methanol and ethanol can be distinguished by heating with iodine and washing soda

$$C_2H_5OH \xrightarrow[Na_2CO_3]{I_2} \underset{\text{Iodoform (yellow ppt)}}{CHI_3} + HCOONa$$

$$+NaI + 2NaOH + H_2O$$

$$CH_3OH \xrightarrow[Na_2CO_3]{I_2} \text{No reaction}$$

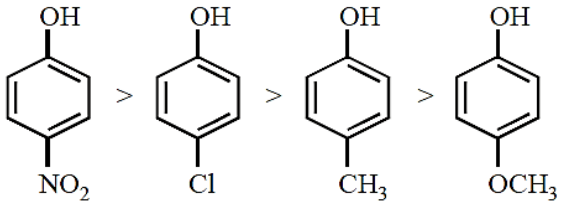
43. (4) The rates of reaction with Lucas reagent follows the order. 3° alcohol > 2° alcohol > 1° alcohol since carbocations are formed as intermediate, more stable the carbocation, higher will be the reactivity of the parent compound (alcohol). 2-Methylpropan-2-ol generates a 3º carbocation, so it will react fastest; other three generates either 1º or 2º carbocations.

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{H^+}$$

2-Methyl-2-propanol

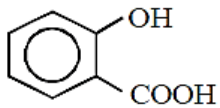
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\overset{|}{\overset{\oplus}{C}}}}} \xrightarrow{Br^-} CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\overset{|}{C}}}}-Br$$

44. 1)
45. 4)
46. 4)
47. 3) Electron withdrawing substituents like $-NO_2$, Cl increase the acidity of phenol while electron releasing substituents like $-CH_3$, $-OCH_3$ decrease acidity. Hence the correct order of acidity will be

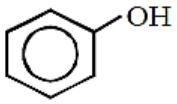


III (–M, –I) > I (–I > +M) > II (+I, + HC) > IV (+ M)

48. (3) Due to strong electron-donating effect of the OH group, the electron density in phenol is much higher than that in toluene, benzene and chlorobenzene and hence phenol is readily attacked by the electrophile.
49. 1)
50. 1)

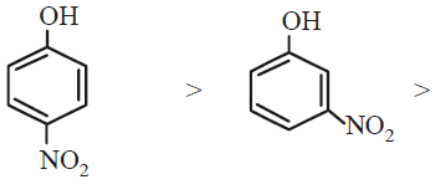


Salicyclic acid (evolves CO_2 with $NaHCO_3$)

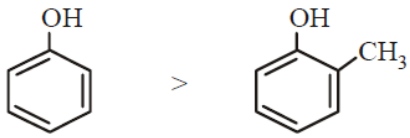


Phenol (No reaction with $NaHCO_3$)

51. (2) Phenol is most acidic because its conjugate base is stabilised due to resonance, while the rest three compounds are alcohols, hence, their corresponding conjugate bases do not exhibit resonance
52. 2)



(iv) (– I and – M effects, both increase acidity) (iii) (only – I effect)



(i) No other group (ii) (+ I effect of CH_3 group decreases acidity)

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

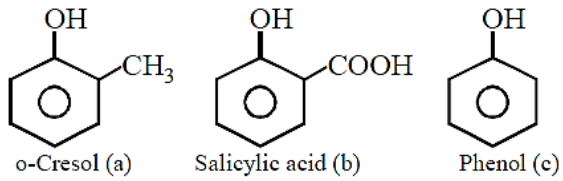
$$R-CH_2-CH_2-OH \xrightarrow[300^\circ C]{Cu} R-CH_2-CHO + H_2$$
1° Alcohol — Aldehyde

$$R-\underset{R}{\overset{H}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[300^\circ C]{Cu} R-\overset{O}{\overset{\|}{C}}-R + H_2$$
2° Alcohol — Ketone

$$R-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH \xrightarrow[300^\circ C]{Cu} R-\underset{CH_3}{\overset{}{\underset{|}{C}}}=CH_2 + H_2O$$
3° Alcohol — Alkene

$$C_6H_5-OH \xrightarrow[300^\circ C]{Cu} \text{No reaction}$$

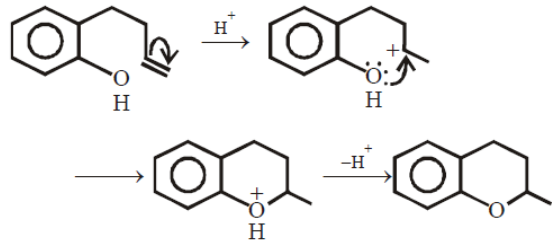
54. 4)



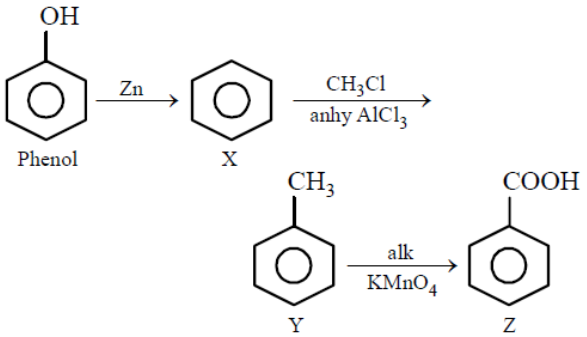
o-Cresol (a) — Salicylic acid (b) — Phenol (c)

Electron releasing groups ($-CH_3$, $-OCH_3$, $-NCH_3$ etc) intensify the negative charge of phenoxide ion, i.e., destablises it hence decreases ionization of parent phenol, therefore decreases acidity. While electron donating groups ($-NO_2$, –COOH, –CHO etc.) increases acidity.

55. 2)



56. 2)



Phenol — X — Y — Z

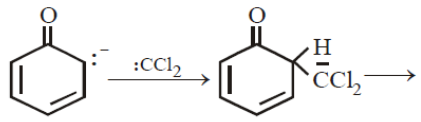
57. 1)

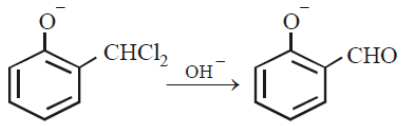
58. 4)

$$HCCl_3 + NaOH \rightarrow NaCl + H_2O + :\bar{C}Cl_3$$

$$\rightarrow \quad :CCl_2 + Cl^-$$

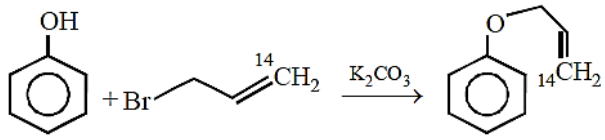
Dichlorocarbene
(a neutral electrophile)

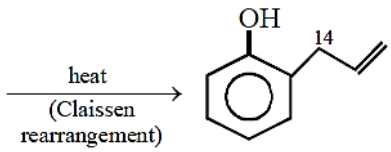




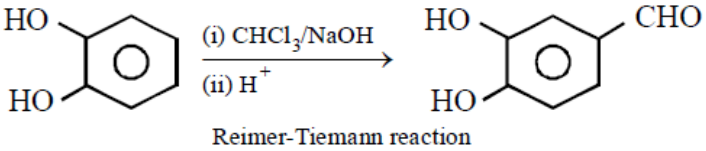
59. 4) Dichlorocarbene is a neutral species, not ionic.

60. 2)

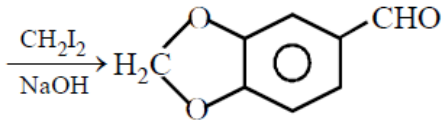




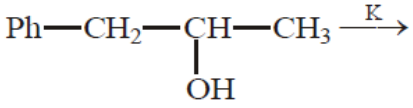
61. 4)

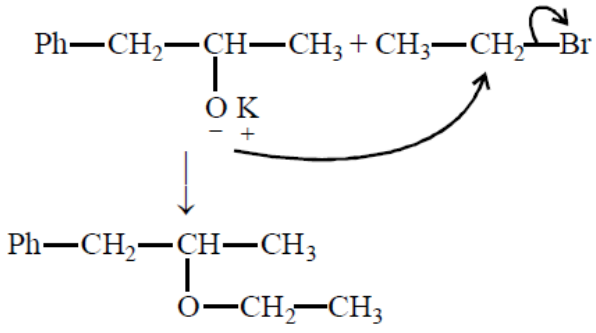


Reimer-Tiemann reaction



62. 2)





63. 1)

$$(CH_3)_2CHO^{-}\overset{+}{Na} + CH_3I \longrightarrow (CH_3)_2CH-O-CH_3 + NaI$$

64. 4) The two components should be $(CH_3)_3CONa + (CH_3)_3CBr$. However, tert-alkyl halides tend to undergo elimination reaction rather than substitution leading to the formation of an alkene, $Me_2C = CH_2$

65. 2)

$(CH_3)_3CBr + NaOC_2H_5$ can't be applied for synthesising the ether because sod. ethoxide, being a strong base, will preferentially cause elimination reaction.

$$(CH_3)_3CBr \xrightarrow{^-OC_2H_5} (CH_3)_2C = CH_2 + HBr$$

In isobutene + ethanol, isobutene will form *tert*-butyl cation which reacts with ethanol, a nucleophile to form ether.

$$(CH_3)_2C = CH_2 \xrightarrow{H^+} (CH_3)_2\overset{+}{C}CH_3$$

$$\xrightarrow[(ii)\ -H^+]{(i)\ CH_3CH_2OH} (CH_3)_3COCH_2CH_3$$

$$C_6H_5ONa + C_2H_5I \xrightarrow{\Delta} \underset{\text{Phenetole}}{C_6H_5OC_2H_5} + NaI$$

66. 1)

67. 2) Williamson's synthesis –

$$CH_3 - CH_2 - ONa + Br - CH_2 - CH_3 \rightarrow$$

$$CH_3 - CH_2 - O - CH_2 - CH_3$$

68. (1) Like dissolves like. Oils and fats, being covalent, dissolve in ether, a non-polar solvent.

69. (2) Reaction of sodium ethoxide with ethyl iodide to produce diethyl ether is known as Williamson synthesis. It is a nucleophilic substitution reaction and proceeds via SN_2 mechanism.

70. 4)

$$C_2H_5 - O - C_2H_5 + O_2 \xrightarrow[25°C]{h\nu}$$

$$CH_3 - CH(OOH) - O - C_2H_5$$

NEET PREVIOUS YEARS QUESTIONS-EXPLANATIONS

1. 3)

$$\underset{(A)}{C_2H_5OH} \xrightarrow{Na} \underset{(B)}{C_2H_5O^-Na^+}$$

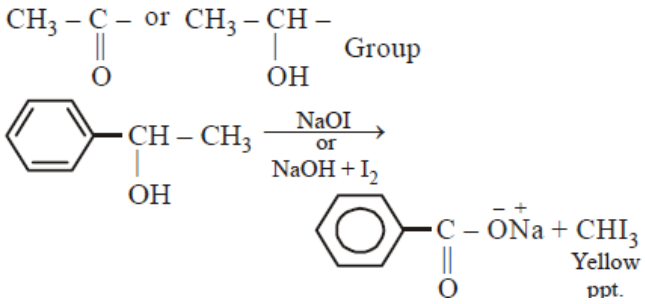
$$\downarrow PCl_5$$

$$\underset{(C)}{C_2H_5Cl}$$

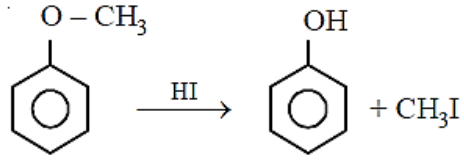
$$\underset{(B)}{C_2H_5O^-Na^+} + \underset{(C)}{C_2H_5Cl} \xrightarrow{S_N2} C_2H_5OC_2H_5$$

So the correct option is 3)

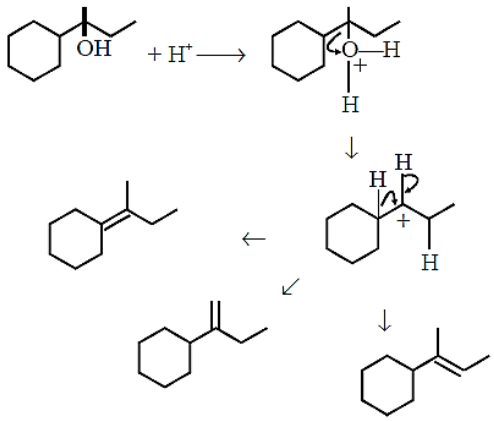
2. 4) Haloform reaction is shown by compound having



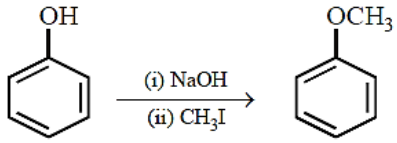
3. 2) When Ar – O – R ethers are reacted with HI, they are cleaved at weaker O – R bond to give phenol and alkyl iodide.



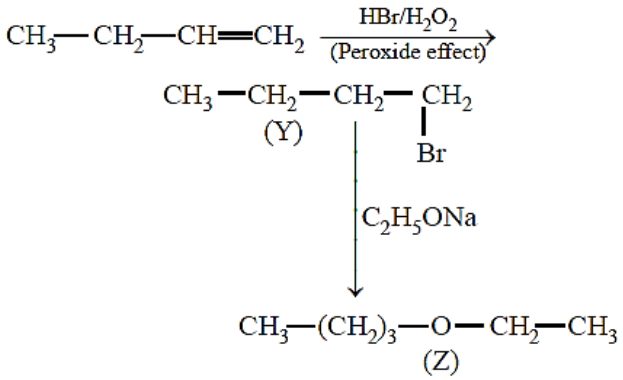
4. (1)
5. (1) This is an example of Williamson ether synthesis reaction in which sodium alkoxide reacts with alkyl halide and gives ether.
6. (4)
7. 2)



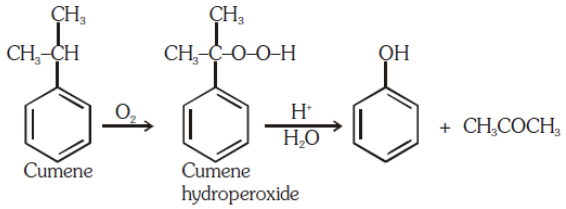
8. (4) Williamson synthesis is one of the best methods for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.
9. (2) Phenols react with alkyl halides in alkaline medium to form ethers. Therefore,

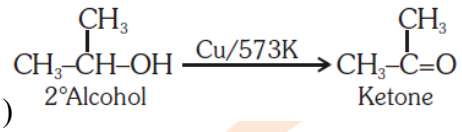


10. (3) *o*-nitrophenol will not be soluble in $NaHCO_3$. Due to intramolecular hydrogen bonding hydrogen on OH is strongly bound. So it can not behave as an acid and can not react with sodium bicarbonate.
11. 1)



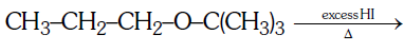
12. 2) Phenol is manufactured from the hydrocarbon, cumene. Cumene (isopropylbenzene) is oxidised in the presence of air to cumene hydroperoxide. it is converted to phenol and acetone by treating it with dilute acid. Acetone, a by-product of this reaction, is also obtained in large quantities by this method.

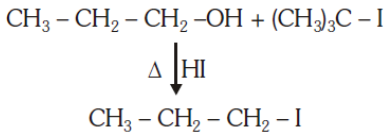




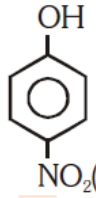
13. 3)

14. 1)



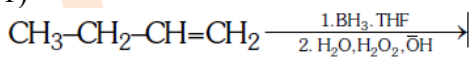


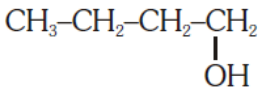
15. 1)



-NO_2group is electron withdrawing group.
Which increases the acidic strength of phenol.

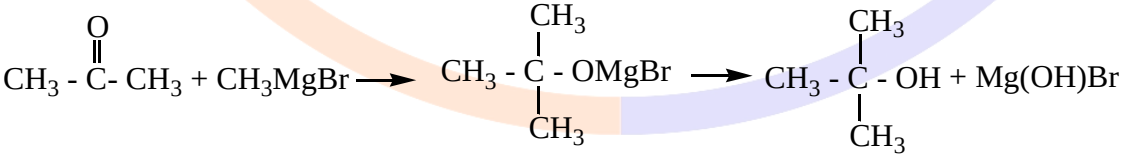
16. 1)



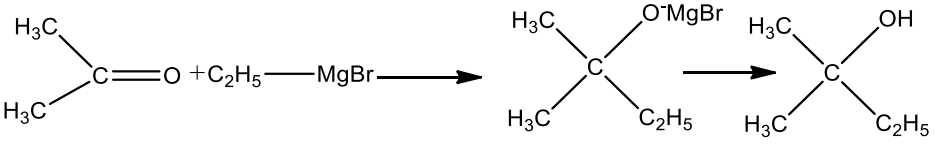


(Hydroboration-oxidation)

17. 4)



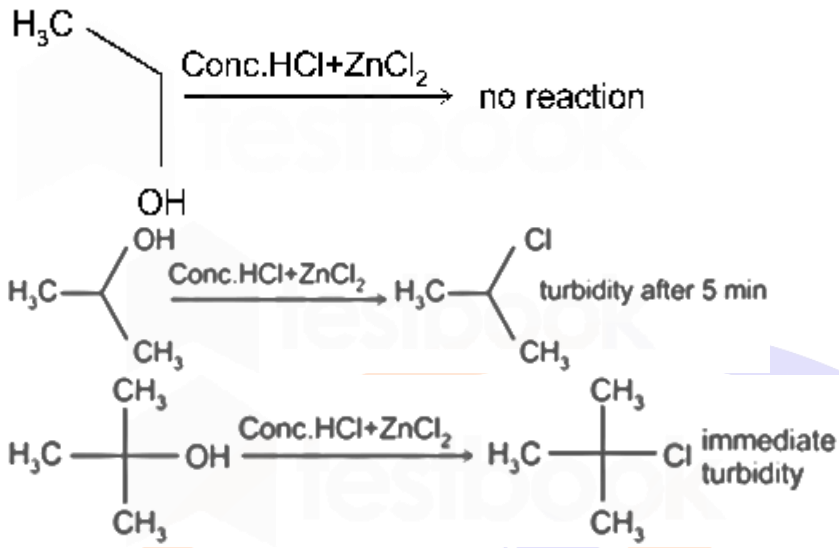
18. 3) (2-methy butan-2-ol)



19. The acidic strength of P – nitrophenol > O-nitrophenol > meta –nitrophenol

20. Statement I is correct but Statement II is Incorrect

The chemical reaction of primary, secondary and tertiary alcohols with lucas reagent is as follows



Hence correct option is Statement I is correct but Statement II is Incorrect