CHAPTER - 19

ALCOHOLS, PHENOLS AND ETHERS

SYNOPSIS

Alcohols : They are hydroxy derivatives of hydrocarbon. They are classified as monohydric, dihydric, trihydric etc depending on the no: of - OH groups per molecule. Monohydric alcohols are classified into primary (1^0), secondary (2^0) and tertiary (3^0) alcohols with characteristic groups $-CH_2OH$, >CHOH and

$\begin{array}{c}|\\ -C-\\ |\end{array}$ OH respectively

Eg: CH_3-CH_2-OH Ethyl alcohol (1^0)

$(CH_3)_2CHOH$ isopropyl alcohol (2^0)

$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$ tert : butyl alcohol (3°)

Isomerism: Alcohols exhibit three types of isomerism viz chain isomerism, position isomerism and functional isomerism

1.Chain Isomerism

Eg. $CH_3CH_2CH_2CH_2OH$ butan-1-ol

$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!\diagdown\!\!\diagup CH.CH_2.OH$

2 methyl propan-1-ol

2. Position isomerism

Eg. $CH_3CH_2CH_2OH$ Propan-1-ol

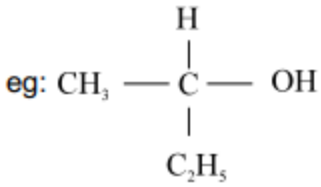
$CH_3CHOH.CH_3$ Propan2-ol

3.Functional isomerism

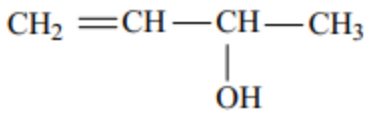
Eg. $CH_3CH_2CH_2OH$ Propan-1-ol

$CH_3CH_2O\,CH_3$ ethyl methyl ether

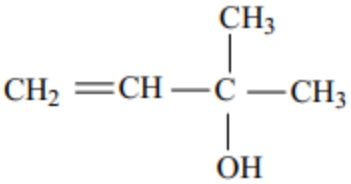
Alcohols having asymmetric carbon exhibit optical isomerism



1. Allylic alcohols : $CH_2 = CH - CH_2 - OH$ (1° allylic)

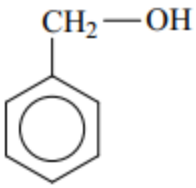


(2° allylic)

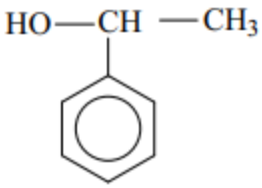


(3° allylic)

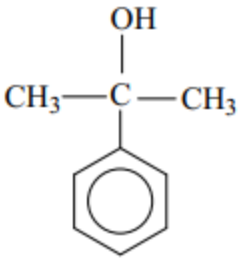
2. Benzylic alcohols :



(1° benzylic)

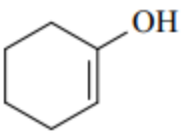


(2° benzylic)



(3° benzylic)

3. Vinylic alcohols (enols) : Eg 1)



2) $CH_2 = CH - OH$

General methods of preparation

1. Hydrolysis of alkyl halides with aqueous alkali or moist Ag_2O

   $C_2H_5Br + KOH\ (aq) \rightarrow C_2H_5OH + KBr$

   $C_2H_5Br + AgOH \rightarrow C_2H_5OH + AgBr$

   The method gives good yield with 1^0 and 2^0 alkyl halides. But 3^0 alkyl halide gives alkene as the main product

2. ***Hydrolysis of ethers***

$C_2H_5 - O - C_2H_5 \rightarrow 2C_2H_5OH$

3. ***Hydrolysis of esters***

$CH_3COOC_2H_5 \rightarrow CH_3COOH + C_2H_5OH$

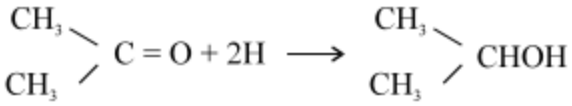
4. ***Action of nitrous acid on 1^0 amines***

$RNH_2 + HONO \rightarrow ROH + N_2 + H_2O$

5. ***Reduction of carbonyl compounds***

Aldehydes, ketones, acid derivatives etc can be reduced to alcohols. The reducing agents usually used are $LiBH_4$, $NaBH_4$, Na/C_2H_5OH, $Li\,AlH_4$ etc

$CH_3CH_2CHO + 2H \rightarrow CH_3CH_2CH_2OH$

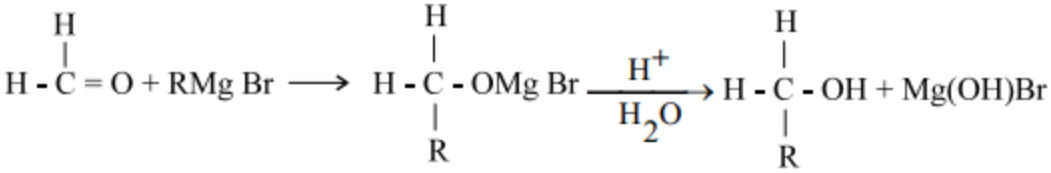


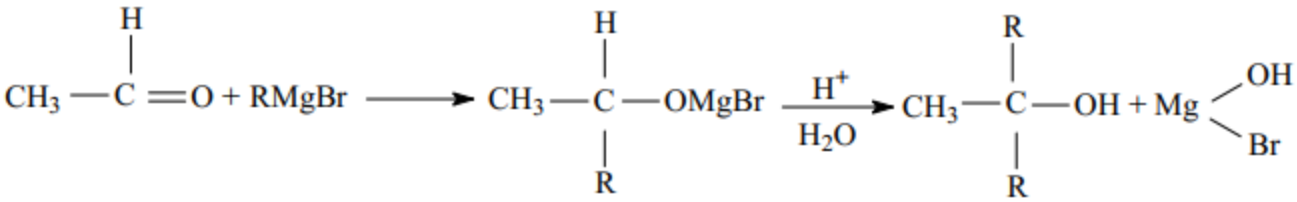
$(CH_3CO)_2O \xrightarrow{Li\,AlH_4} 2CH_3CH_2OH$

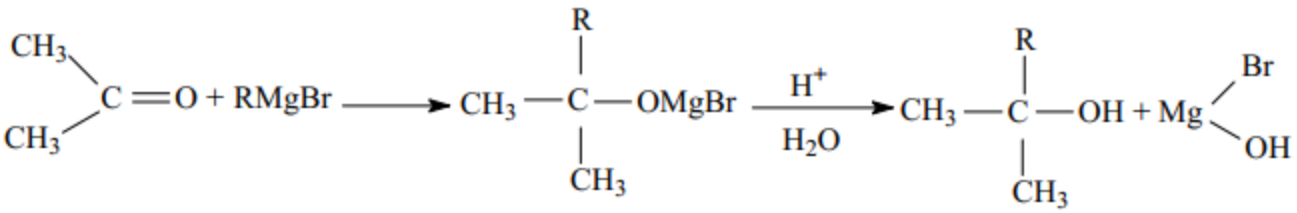
3^0 alcohols cannot be prepared by this method.

6. Grignard reagent gives addition products with aldehydes and ketones which on hydrolysis in acid medium given alcohols.

Formaldehyde gives, 1^0 alcohol while all other aldehydes gives 2^0 alcohols and ketone gives 3^0 alcohols.







7. Fermentation of carbohydrates

$$(C_6H_{10}O_5)_n \xrightarrow{Diastase} \underset{Maltose}{C_{12}H_{22}O_{11}} \xrightarrow{maltase} \underset{glucose}{C_6H_{12}O_6} \xrightarrow{zymase} C_2H_5OH$$
(Starch)

$$\underset{Cane\ sugar\ (molasses)}{C_{12}H_{22}O_{11}} \xrightarrow{invertase} \underset{glucose}{C_6H_{12}O_6} + \underset{fructose}{C_6H_{12}O_6} \xrightarrow{zymase} C_2H_5OH$$

8. **Oxo process**

Alkenes when treated with water gas ($CO+H_2$) in presence of cobalt carbonyl hydride gives aldehydes which on reduction gives alcohols.

$$2CH_3 - CH = CH_2 + 2CO + 2H_2 \xrightarrow{CoH(CO)_4} CH_3 - CH_2CH_2CHO$$

$$\xrightarrow[Zn-Cu]{H} CH_3 - CH_2 - CH_2 - CH_2 - OH$$

9. Alkenes can be converted into alcohols as follows

$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} = CH_2 + H_2O \xrightarrow{H^+} CH_3 - \underset{OH}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}} - CH_3$$ 2 methyl propan - 2- ol

$$CH_3 - CH = CH_2 + Con.H_2SO_4 \xrightarrow{0^oC} CH_3.\underset{OSO_3H}{CH} - CH_3 \xrightarrow[boil]{H_2O} CH_3 - \underset{OH}{CH} - CH_3 + H_2SO_4$$

isopropyl alchol

10. Methanol can be commercially prepared from water gas

$$CO + 2H_2 \xrightarrow[623K]{Cr_2O_3-ZnO} CH_3.OH \text{ methanol}$$

Physical Properties

1. Lower members are colourless liquids. Higher members having more than 12 carbon atoms are wax like solids.
2. They are soluble (miscible) in water and solubility decreases with increase in mole weight.
3. The B.P increases with increase in carbon chain. For isomeric alcohols, the B.P varies in the order $1^0 > 2^0 > 3^0$

Chemical Properties

Reactions involving cleavage of O–H – bond

1. Withe metals they form alcoholates or alkoxides with the liberation of hydrogen. The order of reactivity is $1^0 > 2^0 > 3^0$
2. With mono carboxylic acids they gives esters
   $R\,COOH + R^1OH \rightarrow RCOOR^1$
3. With acid chloride and acid anhydride they forms acetyl derivatives
   $ROH + ClCOR^1 \rightarrow ROCOR^1 + HCl$
   $ROH + (R^1CO)_2O \rightarrow ROCOR^1 + R^1COOH$
4. With dialkyl sulphates they form ethers
   $ROH + R_2^1\,SO_4 \rightarrow ROR^1 + R^1HSO_4$
5. With grignard reagent they form alkane

Reactions involving the cleavage of C – OH bond

1. With halogen acids alcohols gives alkyl halides. The reactivity of halogen acids is in the order HI> HBr> HCl. Reactivity of alcohols is in the order $3^0 > 2^0 > 1^0 < CH_3OH$. Allylic and Benzylic alcohols are as reactive as 3°.
2. With PCl_5 and PCl_3 alcohols gives alkyl halides
3. With NH_3 they form 1^0, 2^0 and 3^0 amines

Reactions involving cleavage of alkyl and hydroxyl group

1. Dehydration : Dehydration of alcohols give alkene

$$CH_3CH_2OH \xrightarrow[350C]{Al_2O_3} CH_2 = CH_2 + H_2O$$

The reactivity of alcohols is in the order $3^0 > 2^0 > 1^0$. In case of 2^0 and 3^0 alcohols saytzeff's rule is followed

2. Dehydrogenation : When vapours of alcohols are passed over red hot copper at 300^0, 1^0 alcohols gives aldehyde, 2^0 gives ketone and 3^0 gives alkene
3. Oxidation: 1^0 alcohols on oxidation gives acids, 2^0 alcohols gives mixture of acids and 3^0 alcohols are stable towards oxidation in neutral and alkaline media, but they can be oxidised in acid medium, on prolonged heating with the oxidising agent.
4. Halogen in aqueous solution : will oxidise 1° alcohols to aldehydes and 2° alcohols to ketones.
5. Halo form reactions : Alcohols which posses $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-$ group connected to C or H, when heated with halogen and sod. hydroxide or aq. sod. carbonate gives haloform.

Eg: $C_2H_5OH + 4\,I_2 + 6NaOH \rightarrow \underset{\text{Iodoform}}{CHI_3} + 5NaI + HCOONa + 5H_2O$

Methyl alcohol does not answer this test

Methods of distinction of 1^0, 2^0 and 3^0 alcohols

1. With Lucas reagent (anhy. $ZnCl_2$ + Con. HCl)

1^0 alcohol gives no turbidity 2^0 alcohol gives turbidity with in 5 minutes

3^0 alcohol gives turbidity immediately

Acid dichromate test

1^0 alcohol	solution turns green
2^0 alcohol	solution turns green
3^0 alcohol	no colour change

Dihydric alcohol

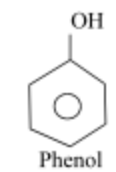
glycol – Ethane 1, 2 diol

Trihydric $\underset{\displaystyle OH}{\underset{|}{CH_2}}-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH_2}}$ (propane 1, 2, 3-triol or Glycerol)

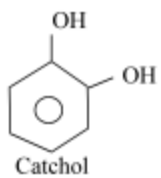
Phenols

Phenols are hydroxyderivatives of aromatics hydrocarbons in which the –OH group is directly attached to the carbon atom of the aromatic ring. Phenol was discovered in the middle oil fraction of coal-tar distillation and named it carbolic acid. Phenols are also classified into monohydric, dihydric and trihydric according to the number of –OH groups per molecule

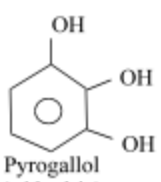
Eg.



Phenol
(mono hydric)

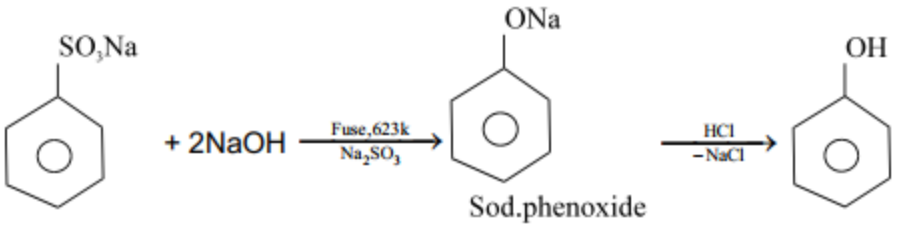


Catchol
(di hydric)

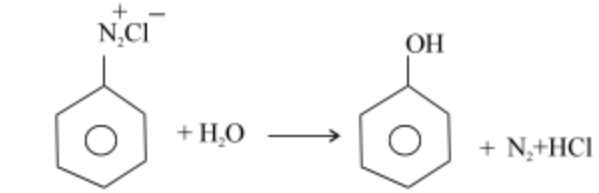


Pyrogallol
(tri hydric)

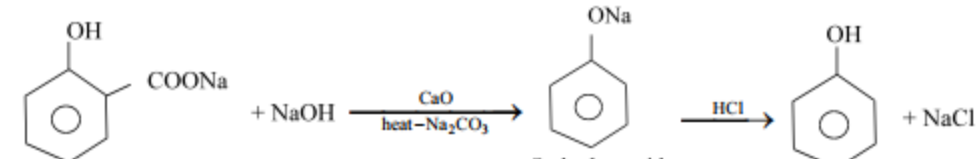
Preparation

1. 

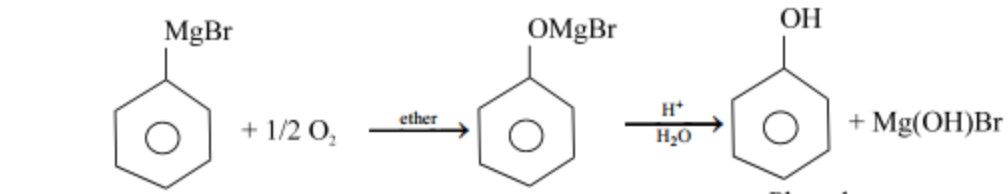
Sod. benzene sulphonate

2. 

Benzene diazonium chloride — Phenol

3. 

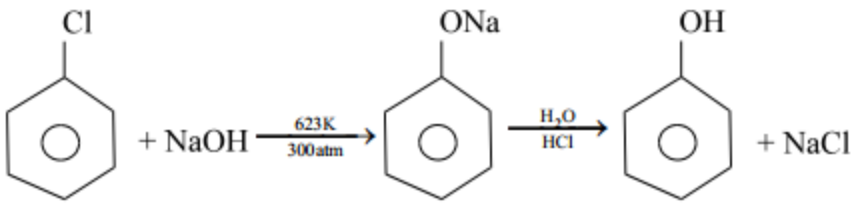
Sod. Salicylate — Sod. phenoxide

4. 

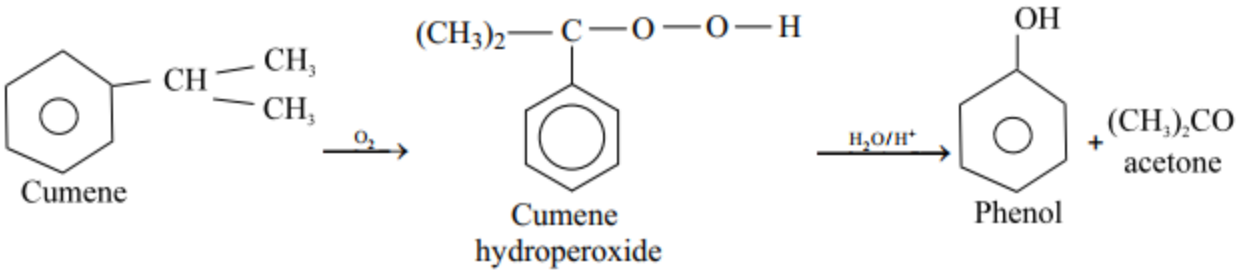
Phenyl magnesium bromide (grignard reagent) — Phenol

Manufacture

1. Dow process



2. Oxidation of cumene

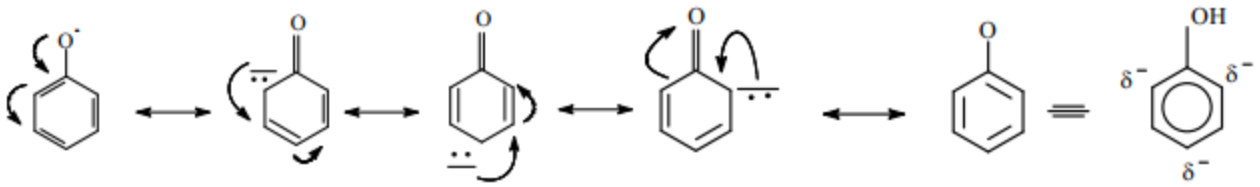


Chemical properties

Acidic nature: Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution

$$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^- + H_3^+O$$

The phenoxide ion is stable due to resonance



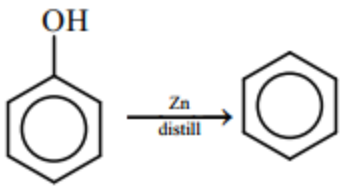
Presence of electron attracting groups (–NO_2, –x, –CN, –CHO etc) increases the acidity of phenol while electron releasing group (–CH_3, –C_2H_5, –OCH_3 etc) decreases the acidity of phenols.

Reactions of OH group

1. **With $FeCl_3$:** Phenol gives violet colouration with neutral $FeCl_3$ due to the formation a coloured complex
2. **Ether formation :** Phenols reacts with alkyl halides in alkali solution to give ether

   $C_6H_5OH + NaOH \rightarrow C_6H_5ONa \xrightarrow{CH_3Cl} C_6H_5OCH_3$ methoxy benzene.
3. **Ester formation :** With acid chlorides and acid anhydrides in alkali, phenol gives esters

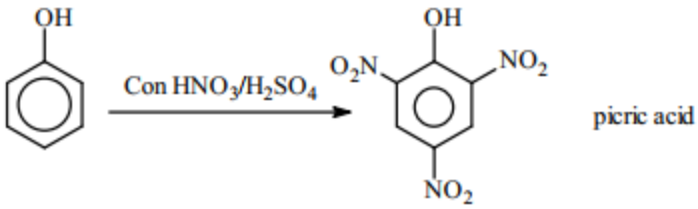
   $C_6H_5ONa + CH_3COCl \rightarrow C_6H_5OCO.CH_3$ Phenyl acetate
4. When distilled with Zin dust phenol gives benzene



Reactions of benzene nucleus

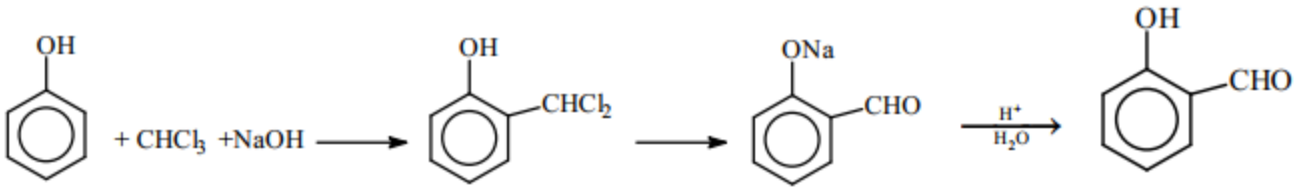
1. (a) Bromination of phenol with Br_2/CS_2 gives a mixture of ortho and para bromo phenol

   (b) With Br_2/H_2O it gives 2, 4, 6 tribromophenol.
2. Nitration with dilute HNO_3 gives a mixture of O and P nitro phenols with Conc. HNO_3/H_2SO_4 2, 4, 6 trinitrophenol (picric acid) is formed



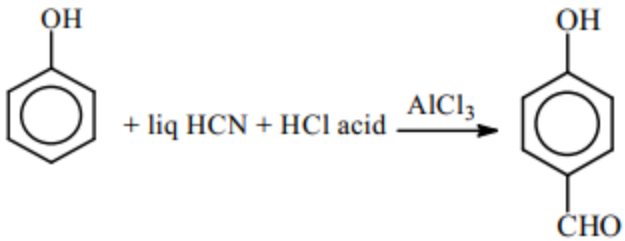
picric acid

3. Reimer : Tiemann reaction



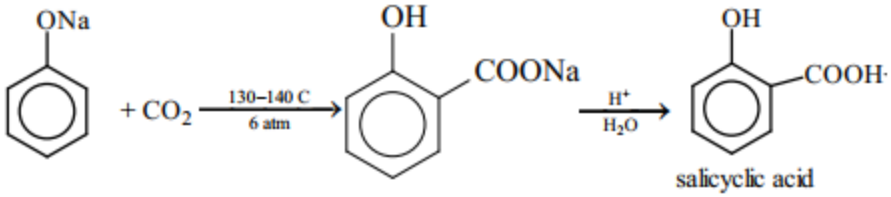
salicyl aldehyde

4. Gattermann's formylation reaction:



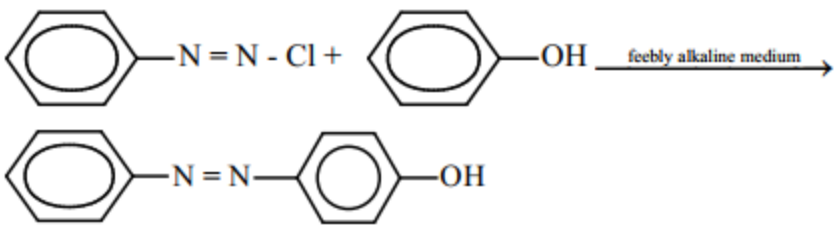
p - hydroxy benzaldehyde

5. Kolbe - Schmidt reaction



salicyclic acid

6. Coupling reactions



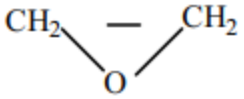
p - hydroxy azobenzene

7. Phenol condenses with HCHO to form Bakelite (resin)

Ethers

Represented by the general formula $R-O-R'$. If R and R^1 are same they are called simple ethers if

they are different then called mixed ethers. They are called as alkoxy alkanes
Eg: $CH_3 - O - CH_3$ - methoxy methane
Eg: $C_2H_5 - O - CH_3$ methoxy ethane



epoxy ethane (Oxirane)

Preparation

1. Dehydration of alcohols

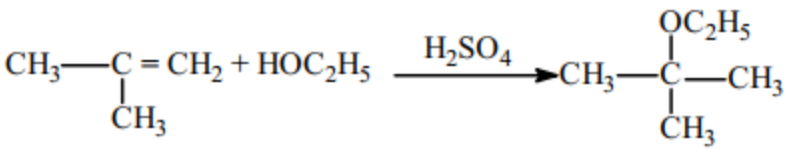
$$C_2H_5OH + HOC_2H_5 \xrightarrow[-H_2O]{\text{Con. } H_2SO_4} C_2H_5 - O - C_2H_5$$

2. Williamson's Synthesis : $C_2H_5ONa + IC_2H_5 \rightarrow C_2H_5 - O - C_2H_5 + NaI$

3. $ROH + CH_2N_2 \xrightarrow{BF_3} R - O - CH_3 + N_2$

diazonomethane

4. Addition of alcohols to alkenes



2 - ethoxy 2 methyl propane

Properties: Properties of ethers are those of alkyl group, lone pair of electrons on oxygen atom, and clevage of C – O bond

1. Peroxide formation : In presence of sunlight ether combines with oxygen to form peroxide

2. Hydrolysis : $C_2H_5 - O - C_2H_5 \xrightarrow{H_2O} 2C_2H_5OH$

Diethyl ether — Ethyl alcohol

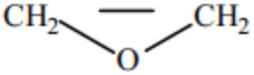
3. With cold HI, ether gives a mixture of alcohol and alkyl iodide

$$C_2H_5OC_2H_5 + HI \xrightarrow{\text{cold}} C_2H_5OH + C_2H_5I$$

When heated with excess of HI, only alkyl iodide is formed

$$C_2H_5 - O - C_2H_5 + 2HI \xrightarrow{\text{heat}} 2C_2H_5I + H_2O$$

Epoxides or Oxiranes

Epoxides are cyclic ethers containing three membered ring eg.  . ethylene oxide or

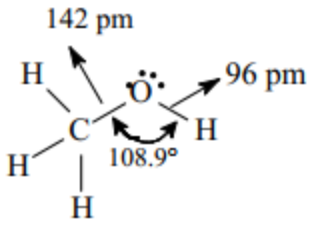
1, 2 epoxy ethane

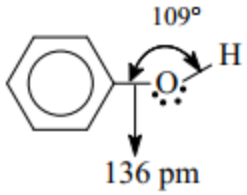
Crown ethers

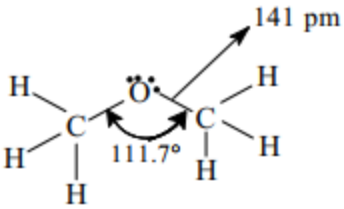
They are macrocyclic polyethers with at least four oxygen atoms.

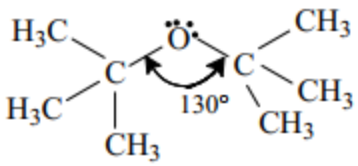
Hybridisation of oxygen in alcohols, phenols and ethers.

Oxygen atom is sp^3 hybridised and there are two lone pairs of electron on the oxygen. The bond angles and bond lengths are as follows





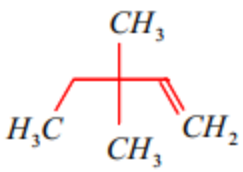




PART-I (JEE MAIN)

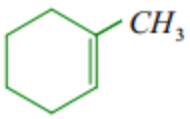
SECTION-I (Straight objective type questions)

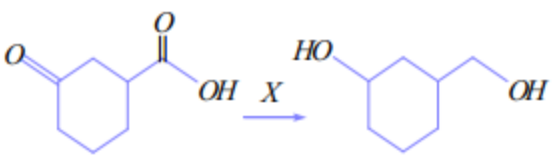
1. Hydroboration-oxidation, oxymercuration-demercuration and acid-catalysed hydration will give the same product in

1) 

2) 

3) 

4) 

2. 

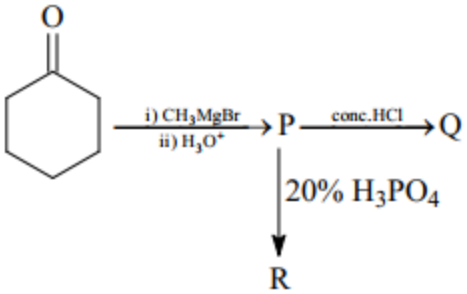
In the above transformation 'X' could be

1) $NaBH_4$

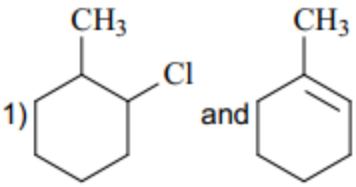
2) $N_2H_4, OH^-, Glycol, \Delta$

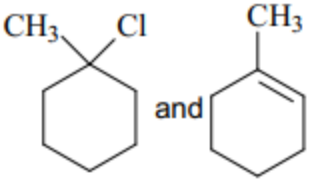
3) $LiAlH_4$

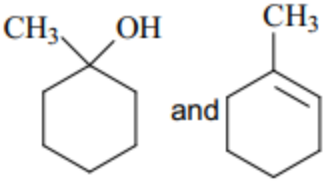
4) DIBAL-H

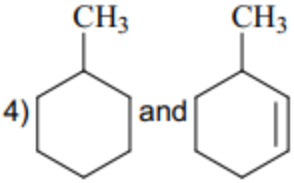
3. 

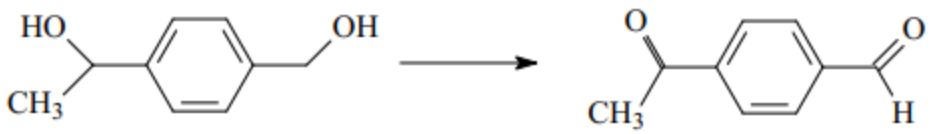
Major products Q and R in the above reaction are

1) 

2) 

3) 

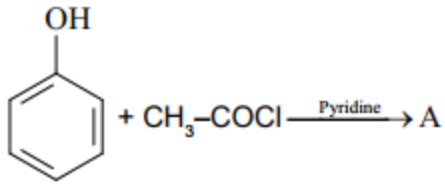
4) 

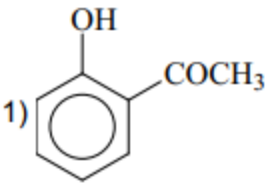
4. 

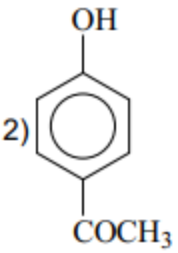
The above transformation can be done by using

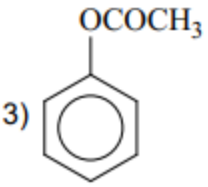
1) Baeyer's Reagent
2) Tollen's reagent
3) Pyridinium chlorochromate
4) Jone's reagent

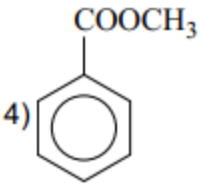
5. The major product 'A' in the following reaction is



1) 

2) 

3) 

4) 

6. Assertion (A) : Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid

Reason (R) : Lewis acid polarizes the bromine molecule

Choose the correct option:

1) Both A and R are correct and R is the correct explanation of A

2) Both A and R are incorrect

3) A is incorrect but R is correct

4) Both A and R are correct but R is not the correct explanation of A

7. Match List-I with List-II

List-I (Reactions)	**List-II (Products)**
I) Phenol + Phthalic anhydride/conc.H_2SO4	P) o-hydroxybenzoic acid
II) Phenol + NaOH/CO_2/H^+	Q) Hydrogen gas
III) Salicylic acid + Acetic anhydride/H^+	R) Phenolphthalein
IV) Tert-butyl alcohol + Al	S) Aspirin

1) $I \rightarrow Q;\ II \rightarrow S;\ III \rightarrow P;\ IV \rightarrow Q$

2) $I \rightarrow R;\ II \rightarrow S;\ III \rightarrow P;\ IV \rightarrow Q$

3) $I \rightarrow R;\ II \rightarrow P;\ III \rightarrow S;\ IV \rightarrow Q$

4) $I \rightarrow Q;\ II \rightarrow P;\ III \rightarrow S;\ IV \rightarrow Q$

8. Reaction of tertiary butyl bromide with sodium methoxide produces mainly

1) Sodium tert-butoxide 2) Tert-butyl methyl ether

3) Isobutane 4) Isobutene

9. Tertiary butyl ethyl ether can be prepared by

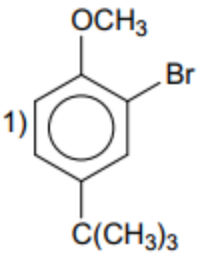
1) Treating tertiary butyl bromide with sodium ethoxide

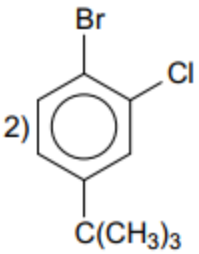
2) Treating sodium tertiary butoxide with methyl bromide

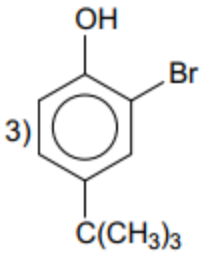
3) Treating sodium tert-butoxide with ethyl bromide

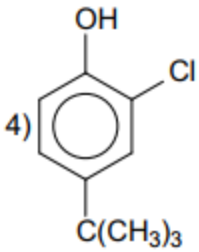
4) Both 1 and 3

10. Anisole $\xrightarrow[AlCl_3]{(CH_3)_3C-Cl}$ X $\xrightarrow{Cl_2/FeCl_3}$ Y $\xrightarrow[\Delta]{HBr}$ Z. The compound Z is

1) 

2) 

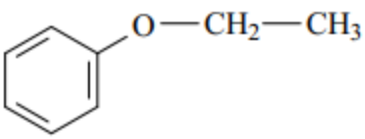
3) 

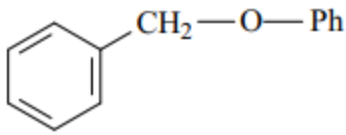
4) 

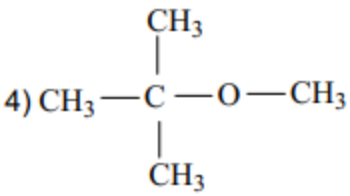
SECTION-II (Numerical Type Questions)

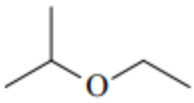
11. How many of the following ethers react with conc. HBr by S_N1 pathway?

1) $CH_3–CH_2–O–CH_3$

2) 

3) 

4) 

5) 

12. A solution of phenol in chloroform when treated with aqueous NaOH gives P as the major product. The mass percentage of carbon in P is ..... (Given atomic mass of C = 12, H = 1, Cl = 35.5 and O = 16)

13. To synthesise one mole of 2-methylpropan-2-ol from ethyl ethanoate, the number of moles of CH_3MgBr required is .....

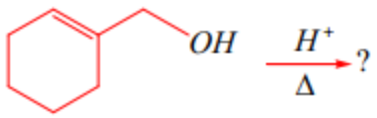
14. How many grams of Br_2 will be required to convert 8 g of phenol into 2,4,6-tribromophenol? (Given atomic mass of Br = 80, C = 12, H = 1 and O = 16)

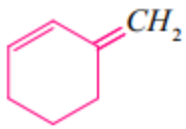
15. A polyhydric alcohol of molecular weight 182 on acetylation gave a product with molecular weight 434. Number of –OH groups in the alcohol is .....

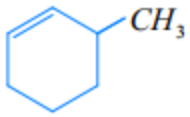
PART-II (JEE ADVANCED)

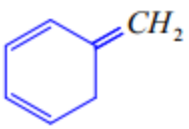
Section-III - Only one option correct type

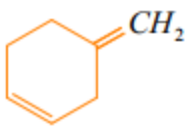
16. Identify the major product in the following reaction



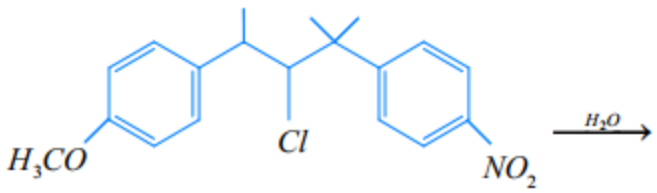
A) 

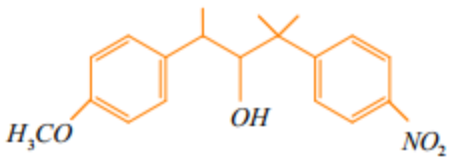
B) 

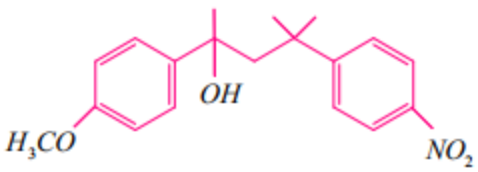
C) 

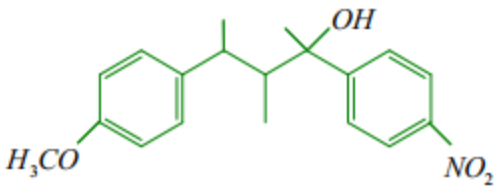
D) 

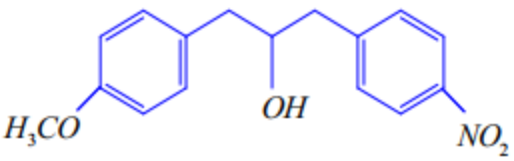
17. Major product formed in the following reaction is



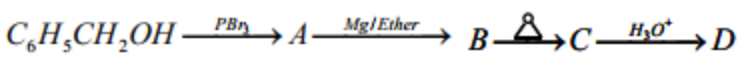
A) 

B) 

C) 

D) 

18. The end product D in the following reaction sequence is



A) $C_6H_5CH_2OCH_2CH_3$

B) $C_6H_5CH(OH)CH_2CH_2OH$

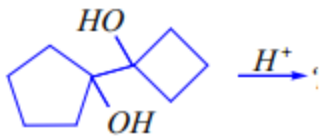
C) $C_6H_5CH_2CH_2CH_2OH$

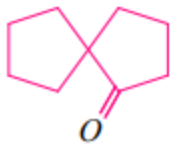
D) $C_6H_5CH_2CH_2OCH_3$

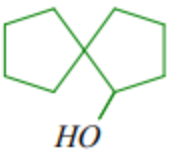
19. A compound (molecular formula $C_6H_{12}O$) does not react with Br_2 in CCl_4, produces a flammable gas on treatement with $LiAlH_4$, and reacts with H_2CrO_4 changing the colour from orange to green. Which of the following compounds best agrees with these facts?

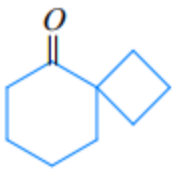
A) 1-Methylcyclopentanol
B) Methoxycyclopentane
C) Hex-4-en-3-ol
D) 2-Cyclobutylethanol

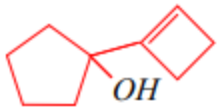
20. What is the major product of the following reaction?



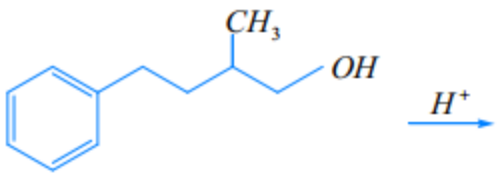
A) 

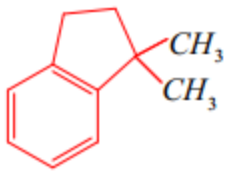
B) 

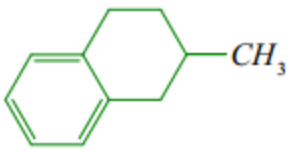
C) 

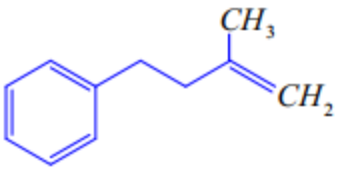
D) 

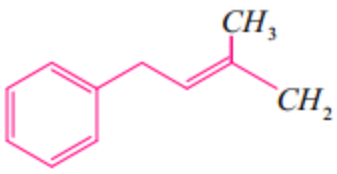
21. Identify the major product of the following reaction



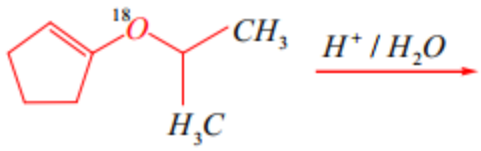
A) 

B) 

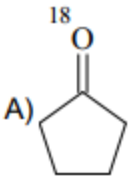
C) 

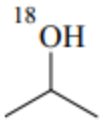
D) 

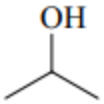
Section IV - One or more option correct type

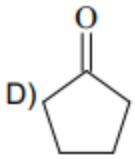
22. 

Product(s) formed in the above reaction is/are

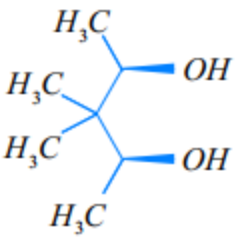
A) 

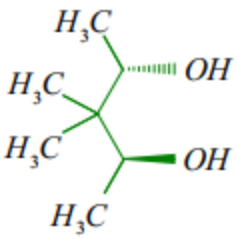
B) 

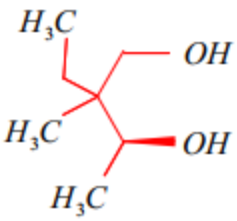
C) 

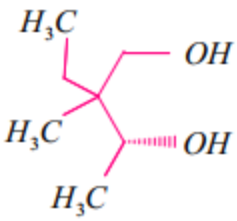
D) 

23. A chiral diol ($C_7H_{16}O_2$) is oxidized by PCC in CH_2Cl_2 to an achiral compound ($C_7H_{12}O_2$). Which of the following would not satisfy these facts?

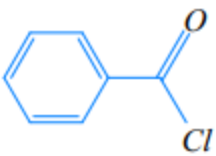
A) 

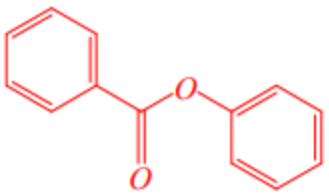
B) 

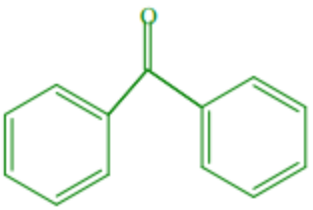
C) 

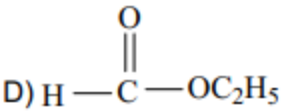
D) 

24. Which of the following would give tertiary alcohol when treated with an excess of CH_3MgBr followed by hydrolysis?

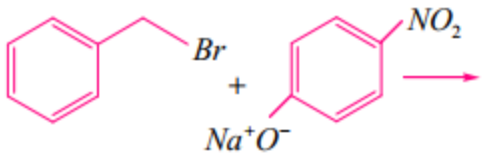
A) 

B) 

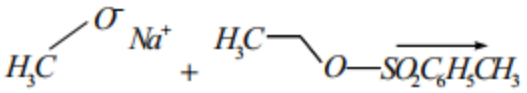
C) 

D) 

25. Which of the following methods is/are useful for the synthesis of ether?

A) 

B) $CH_3CH_2O^-Na^+ + (CH_3)_2SO_4 \rightarrow$

C) 

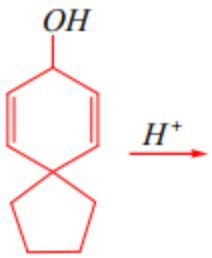
D) $(CH_3)_3CBr + CH_3CH_2ONa \rightarrow$

26. Boiling point of dimethyl ether is greater than that of

A) Ethane B) Propane C) Ethanol D) Chloroethane

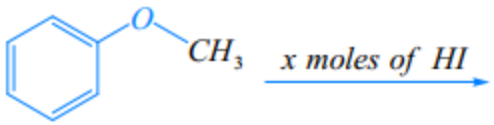
Section V - Numerical type questions

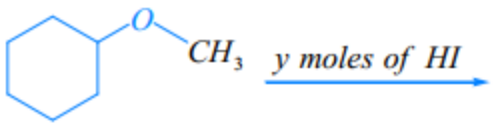
27. The number of six membered ring(s) present in the major product of the following reaction is .....



28. How many of the following compounds would give turbidity with lucas reagent without heating?

1) Benzyl alcohol 2) Allyl alcohol 3) Cyclohexanol 4) 2-Methyl-2-propanol
5) Neopentyl alcohol 6) Phenol 7) o-Cresol
8) Cylopropyl methyl carbinol 9) p-Nitrobenzyl alcohol

29. 



x and y are the maximum number of moles of HI that can react with the compounds shown above. Sum of x and y is

Section-VI - Matrix match type

30. Match the following

Column-I (Compound)	Column-II (pKa)
I) o-Nitrophenol	P) 8.3
II) o-Cresol	Q) 7.2
III) p-Nitrophenol	R) 10.2
IV) m-Nitrophenol	S) 7.1

A) $I \rightarrow Q;\ II \rightarrow R;\ III \rightarrow S;\ IV \rightarrow P$

B) $I \rightarrow S;\ II \rightarrow R;\ III \rightarrow Q;\ IV \rightarrow P$

C) $I \rightarrow Q;\ II \rightarrow P;\ III \rightarrow S;\ IV \rightarrow R$

D) $I \rightarrow S;\ II \rightarrow P;\ III \rightarrow Q;\ IV \rightarrow R$