ALCOHOL
PHENOL
ETHER

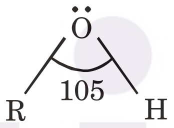
ALCOHOLS

1. Physical Properties :

- The polar nature of the O-H bond (due to the electronegativity different of the atoms) results in the formation of hydrogen bonds with other alcohols molecules or other H-bonding systems (e.g. water). The implications of this are :
  - High melting and boiling points compared to analogous alkanes
  - High solubility in aqueous media

2. Structure :

- The alcohol functional group consists of an O atom bonded to a C atom and a H atom via σ bonds.
- Both the C-O and the O-H bonds are polar due to the high electronegativity of the O atom.
- Alcohols are bent shaped molecules. The central 'O' atom is also sp^3 hybridised and the C-O-H bond angle is 105 .

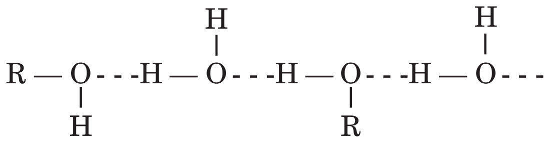


3. Reactivity :

- The alcohol O atom are a region of high electron, density due to the lone pairs.
- Alcohol oxygen atoms are Lewis bases.
- So alcohols can react as either bases or nucleophiles at the oxygen.
- There is low electron density on H atom of the O-H group alcohol, i.e. H^+ character.
- So alcohols are acidic (pKa ~ 16).
- The -OH group is a poor leaving group and needs to be converted to a better leaving group before substitution can occur.

4. Solubility of alcohols :

The first three members are completely miscible with water. The solubility rapidly decreases with increase in molecular mass. The higher members are almost insoluble in water but are soluble in organic solvents like benzene, ether etc. The solubility of lower alcohols is due to the existence of hydrogen bonds between water and polar -OH group of alcohol molecules.Phenols too are sparingly soluble in water. The -OH group in alcohols contains a hydrogen bonded to an electronegative oxygen atom. Thus they form hydrogen bonds with water molecules.



The solubility of alcohols in water decreases with increase in molecular mass because greater carbon content makes alcohol less hydrophilic. In addition, among the isomeric alcohols, the solubility increases with branching of chain. As the surface area of the non-polar part in the molecule decreases, the solubility increases.

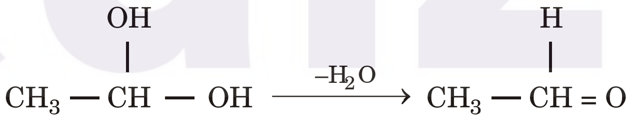
5. Acidity :

- Due to the electronegativity of the O atoms, alcohols are slightly acidic
- The anion derived by the deprotonation of an alcohol is the **alkoxide.**
- Alkoxides are important bases in organic chemistry.
- Alcohols react with Na (or K) like water to give the alkoxide :

$$2\ \text{R–O–H} + 2\ \text{Na} \longrightarrow 2\ \text{NaOR} + \text{H}_2$$

$$2\ \text{H–O–H} + 2\ \text{Na} \longrightarrow 2\ \text{NaOH} + \text{H}_2$$

NOTE : Alcohols containing more than one –OH group linked to the same carbon atom are highly unstable and lose water to form more stable aldehydes or ketones.

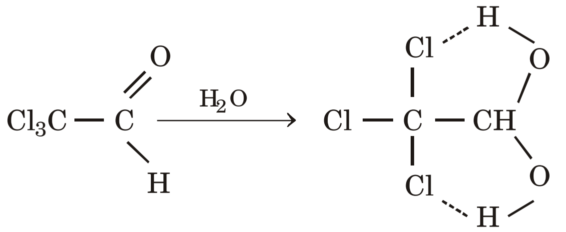


$$\text{CH}_3-\overset{\overset{\text{OH}}{|}}{\text{CH}}-\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3-\overset{\overset{\text{H}}{|}}{\text{CH}}=\text{O}$$

Unstable Ethanal

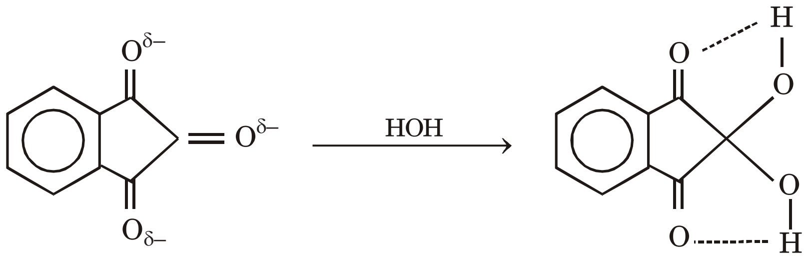
EXCEPTION : Few exception to the above point can be noted.

(1)



In this compound, owing to the presence of hydrogen bonding, alcoholic content is found to be considerably higher.

(2)



minhydrin hydrate

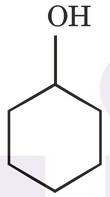
Classification of alcohols :

(1) **Monohydric alcohols** → only one –OH group is present.

For example

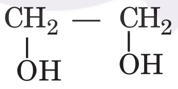
$CH_3\ CH_3\ OH$

Ethanol



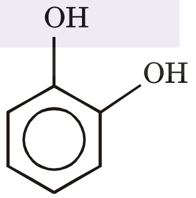
Cyclohexanol

(2) **Dihydric alcohol :** two –OH groups are present in same molecule.



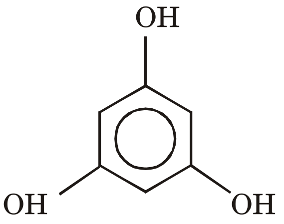
$$\underset{OH}{CH_2} — \underset{OH}{CH_2}$$

1, 2-Ethanediol or
Ethylene glycol



1,2-Dihydroxy benzene
or catechol

(3) **Trihydric alcohols :** three –OH groups present.



1,3,5-Trihydroxy benzene
or phloroglucinol

$$\underset{OH}{CH} — \underset{OH}{CH} — \underset{OH}{CH_2}$$

Glycerol

Example 1

Explain the following :

(a) When equal volumes of ethanol and water are mixed, the total volume is less than the sum of the two individual volumes.

(b) Propanol (MW = 60) has a higher boiling point than butane (MW = 58)

Solution :

(a) The water solubility of alcohols is attributed to intermolecular H-bonding with H_2O. As the molecular weights of the alcohols increase, their solubility in water decreases, because greater carbon content makes the alcohols less hydrophilic. Conversely, their solubility in hydrocarbon solvents increases.

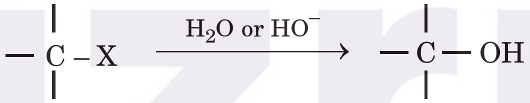
(b) H–bonding between ethanol and water molecules.

(c) Alcohol molecules attract each other by relatively strong H–bonds and somewhat weaker dipole – dipole interactions, resulting in a higher bp. In alkanes only weaker van der Waals' attractive force must be overcome to vaporize the hydrocation.

PREPARATION OF R-OH

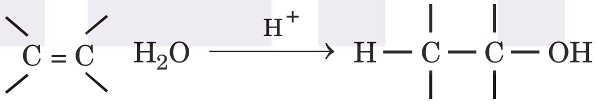
A summary of all the methods of preparation is given below.

Hydrolysis of Alkyl Halides

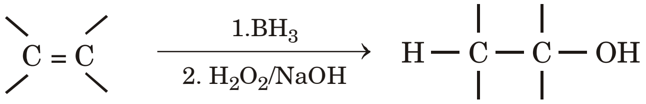


$$-\overset{|}{\underset{|}{C}}-X \xrightarrow{H_2O \text{ or } HO^-} -\overset{|}{\underset{|}{C}}-OH$$

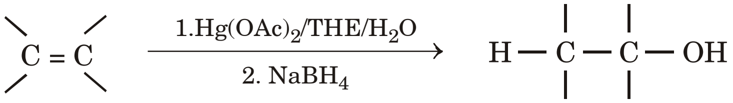
Hydration of Alkenes



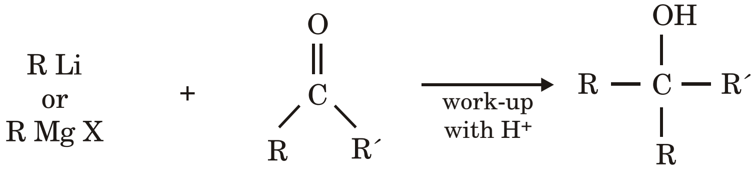
Hydroboration-Oxidation of Alkenes



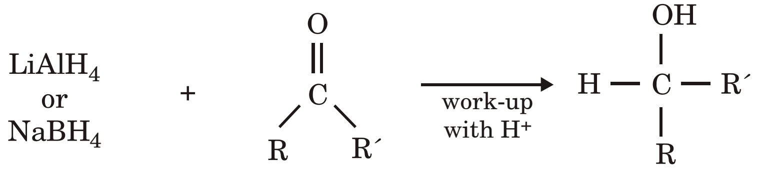
Oxymercuration Demercuration of Alkenes



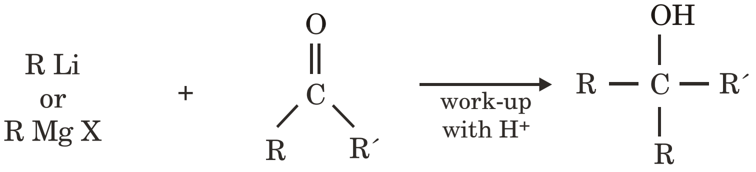
Organometallics with Aldehydes and Ketones



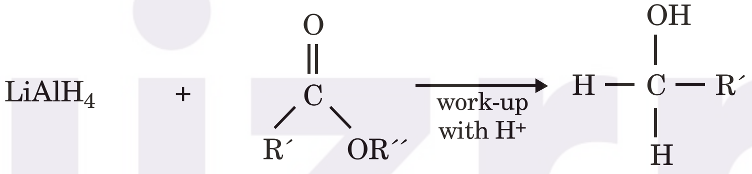
Reduction of Aldehydes and Ketones



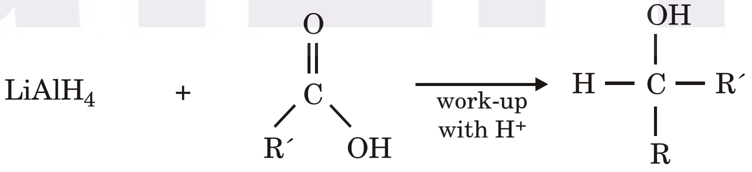
Organometallics with Esters



Reduction of Esters



Reduction of Carboxylic Acids



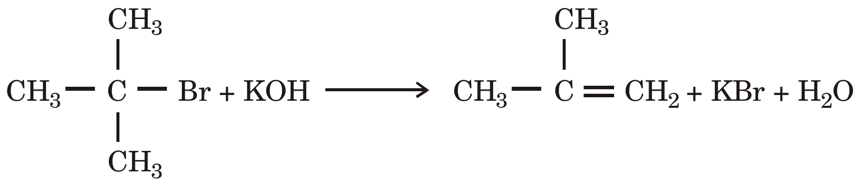
Opening Epoxides

1. From alkyl Halides

Alkyl halides when boiled with aqueous solution of KOH or moist silver oxide furnish alcohols.

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

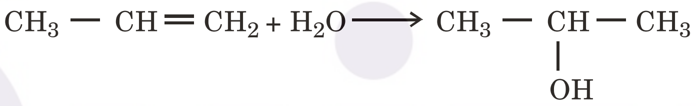
Primary alkyl halides give good yield of alcohols. However, tertiary alkyl halides mainly undergo dehydrohalogenation resulting in formation of alkenes.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br + KOH \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + KBr + H_2O$$

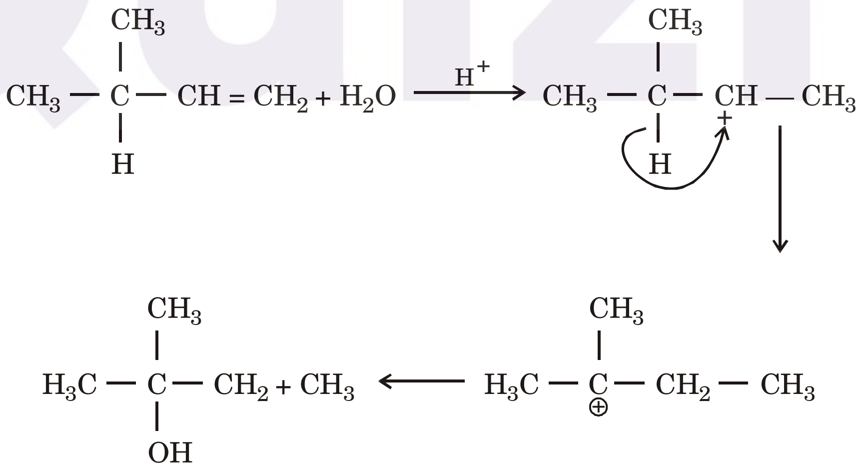
2. FROM ALKENES

2.1 Hydration of Alkenes



$$CH_3-CH=CH_2 + H_2O \longrightarrow CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

MECHANISM :



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-\overset{+}{CH}-CH_3$$

$$\downarrow$$

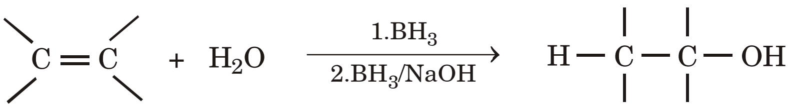
$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2 + CH_3 \longleftarrow H_3C-\overset{\overset{CH_3}{|}}{\underset{\oplus}{C}}-CH_2-CH_3$$

Some points :

(1) Addition is predicted by Markonikov's rule

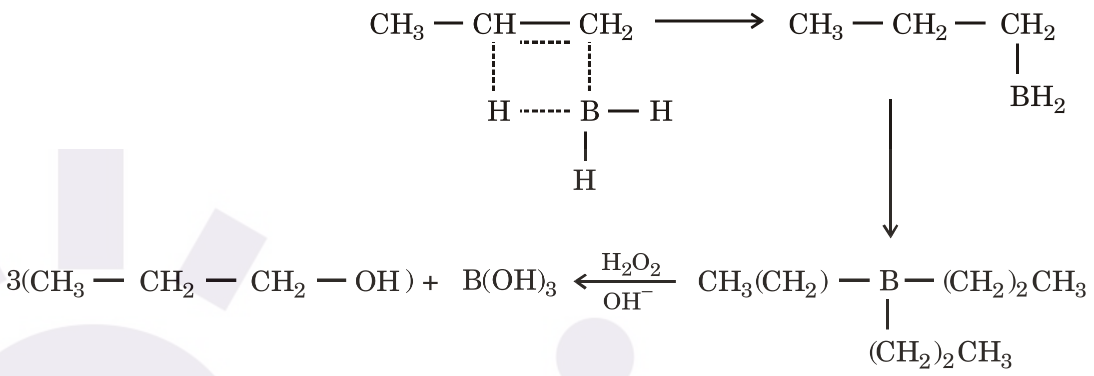
(2) Reaction proceeds via protonation to give more stable carbocation intermediate.

2.2 Hydroboration / oxidation of Alkenes



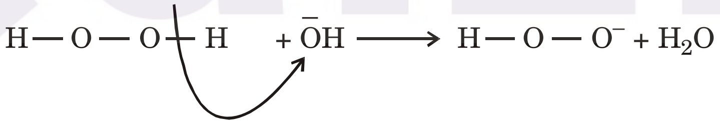
Alkenes react with diborane to form trialkyl boranes, which upon treatment with alkaline H_2O_2 give alcohols via anti-Markowni koff's addition of water. **Also, it is a 'syn' reaction.**

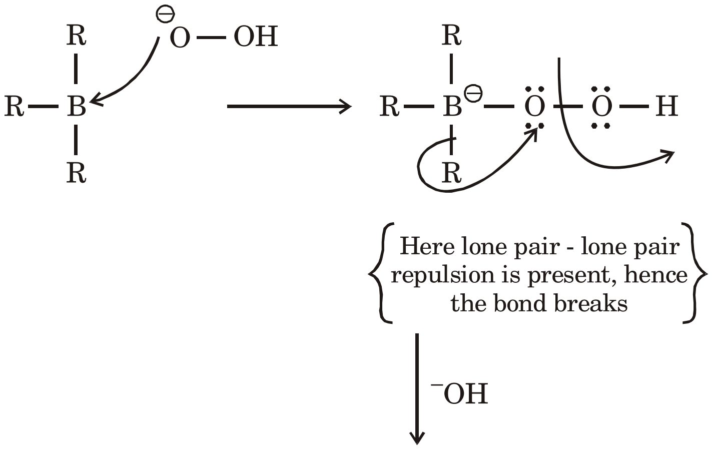
Mechanism :



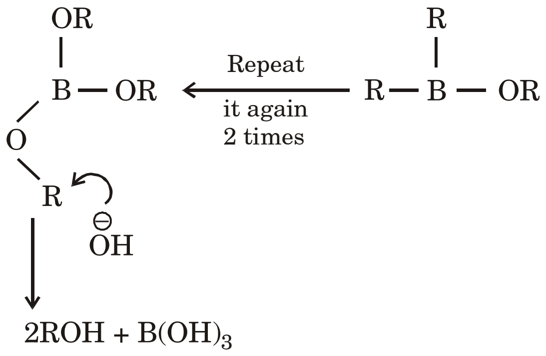
Now, let us also see the mechanism of the following reaction.

$$R_3B \xrightarrow[H_2O_2]{NaOH} 3ROH + B(OH)_3$$



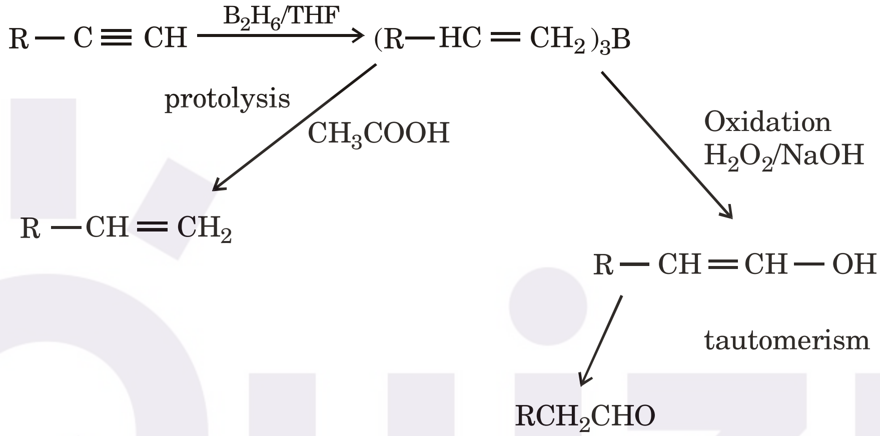


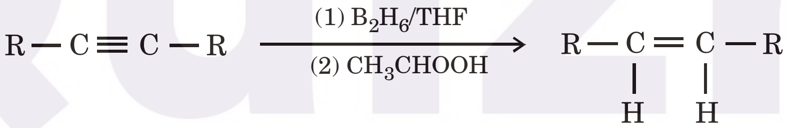
Here lone pair - lone pair repulsion is present, hence the bond breaks



Some Important Points :

(1)



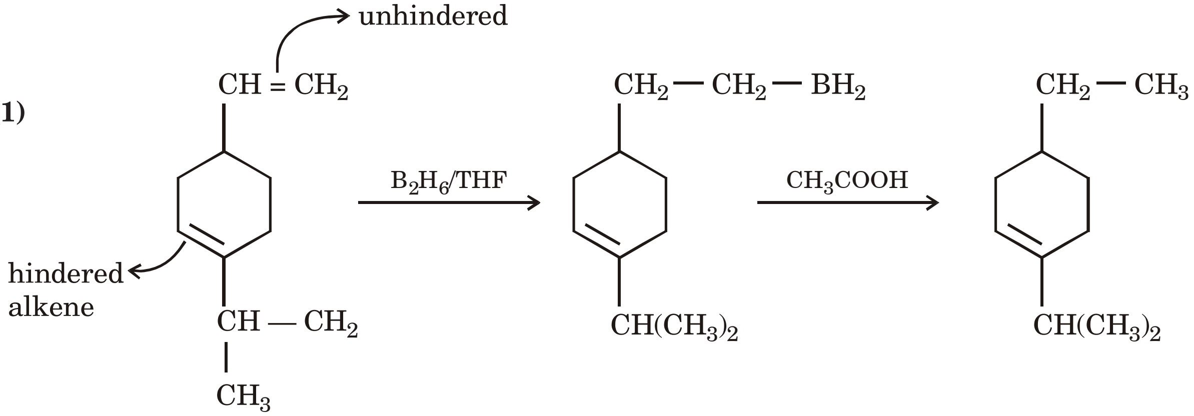


$$R-C\equiv C-R \xrightarrow[\text{(2) CH}_3\text{CHOOH}]{\text{(1) B}_2\text{H}_6\text{/THF}} \underset{\displaystyle H}{\underset{|}{R-C}}=\underset{\displaystyle H}{\underset{|}{C-R}}$$

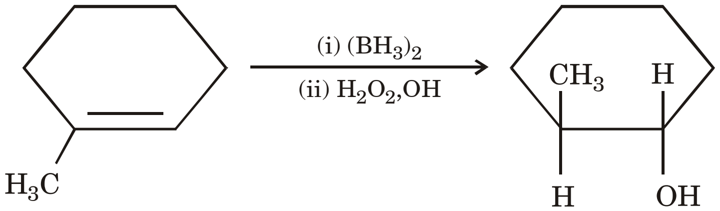
(2) Double bond can also be selectively reduced by B_2H_6/THF at the least hindered position.

For example :

(1)



(2)

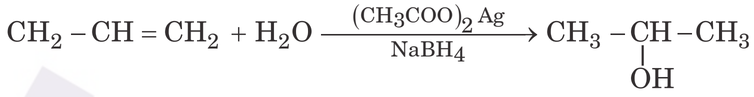


1-methyl cyclopentene

2-methyl cyclopentene
syn-addition

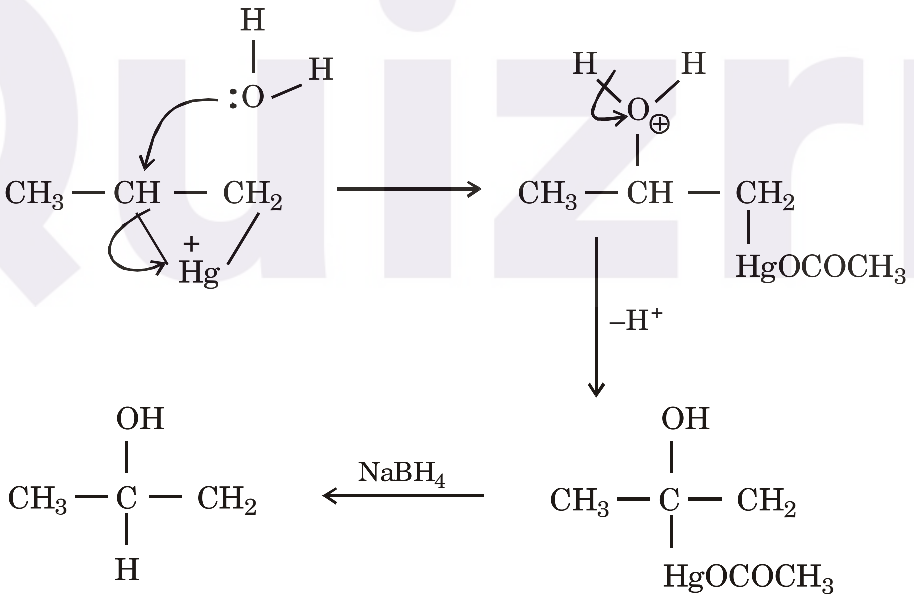
2.3 By oxymercuration-dimercuration

Alkenes can be converted into alcohols by **oxymercuration-demercuration** reaction. In this reaction, addition of water takes place according to Markownikoff's rule.



$$CH_2-CH=CH_2+H_2O\xrightarrow[NaBH_4]{(CH_3COO)_2\,Ag}CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

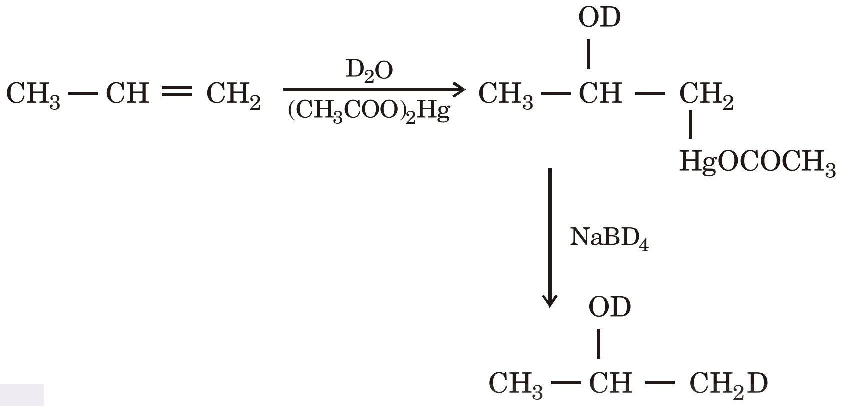
Mechanism :



Example 2

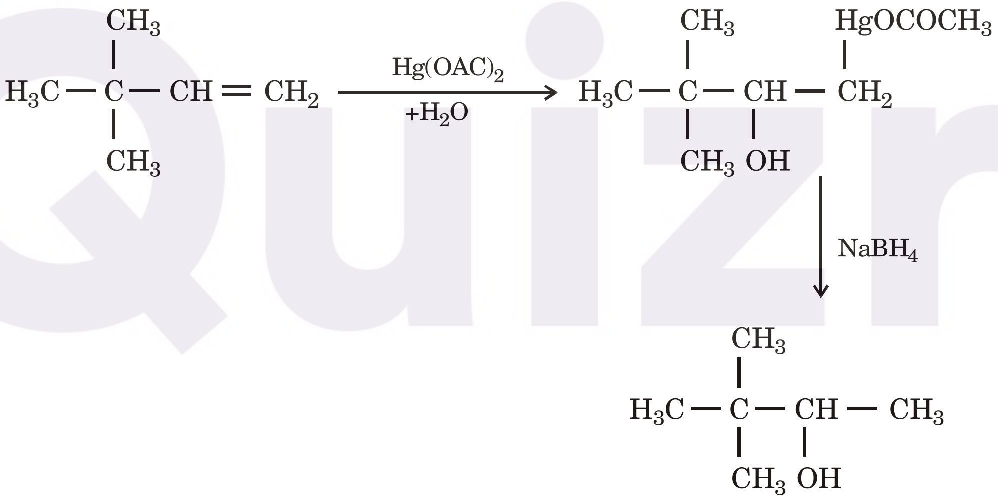
$$CH_3-CH_2=CH_2 \xrightarrow[NaBD_4]{D_2O,(CH_3COO)_2\ Hg} ?$$

Solution :



$$CH_3-CH=CH_2 \xrightarrow[(CH_3COO)_2Hg]{D_2O} CH_3-\overset{\overset{OD}{|}}{CH}-\underset{\underset{HgOCOCH_3}{|}}{CH_2} \xrightarrow{NaBD_4} CH_3-\overset{\overset{OD}{|}}{CH}-CH_2D$$

Example 3



$$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow[+H_2O]{Hg(OAC)_2} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{CH}-\overset{\overset{HgOCOCH_3}{|}}{CH_2} \xrightarrow{NaBH_4} H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{OH}{|}}{CH}-CH_3$$

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3. FROM ALDEHYDES AND KETONES

3.1 By using Grignard Reagents

When a solution of an alkyl halide in dry ethyl ether, $(C_2H_5)_2O$, is allowed to stand over turnings of metallic magnesium, a vigorous reaction takes place. The resulting solution is known as **Grignard reagent.** It is one of the most useful and versatile reagents known.

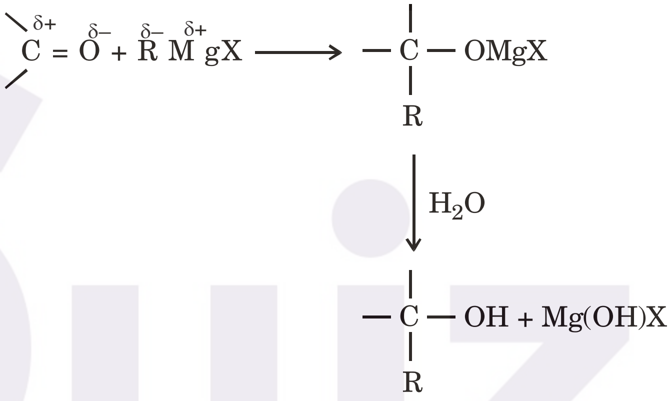
$$\underset{\text{Alkyl halide}}{RX} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Alkyl magnesium halide}}{R\ MgX}$$

The carbon-magnesium bond is covalent but highly polar, with carbon pulling away electrons from electropositive magnesium but the magnesium-halogen bond is essentially ionic, $\overset{\ominus}{R}\,\overset{\oplus}{M}gX$

The Grignard reagent belongs to a class of compounds called organometallic compounds, in which carbon is bonded to a metal like lithium, potassium, sodium, zinc, mercury etc. Each kind of organometallic compound has its own set of properties

But whatever the metal, it is electro negative than carbon and the carbon metal bond is always highly polar. Although the organic group is not a full fledged carbanion but has considerable carbanionic character. The, organometallic compounds can serve as a source of carbon bearing negative charge.

So, when Grignard reagent is added to carbonyl compounds, the organic group attaches to carbon and magnesium to oxygen.



$$>\overset{\delta+}{C}=\overset{\delta-}{O}+\overset{\delta-}{R}\,\overset{\delta+}{M}gX \longrightarrow -\underset{R}{\overset{|}{\underset{|}{C}}}-OMgX \xrightarrow{H_2O} -\underset{R}{\overset{|}{\underset{|}{C}}}-OH+Mg(OH)X$$

$$Mg(OH)X \xrightarrow{HX} MgX_2 + H_2O$$

Products formed by Grignard synthesis :

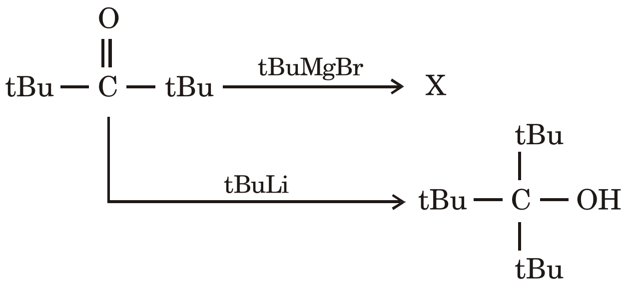
(a) Formaldehyde yields primary alcohol

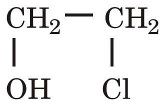
(b) Any other aldehyde yields secondary alcohol.

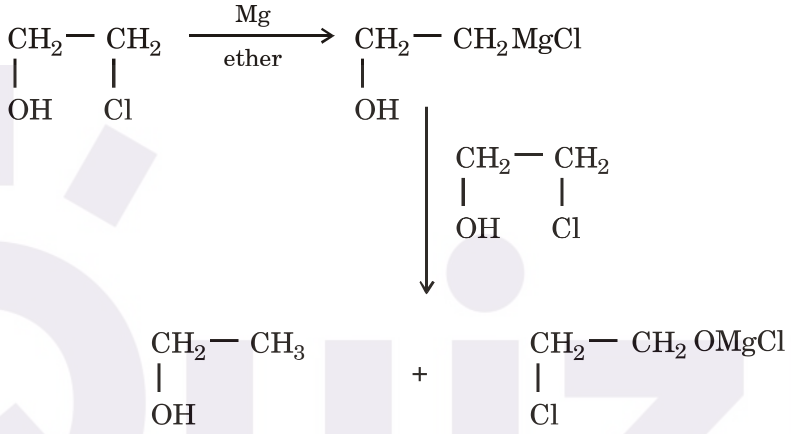
(c) Ketones yield tertiary alcohols.

NOTE :

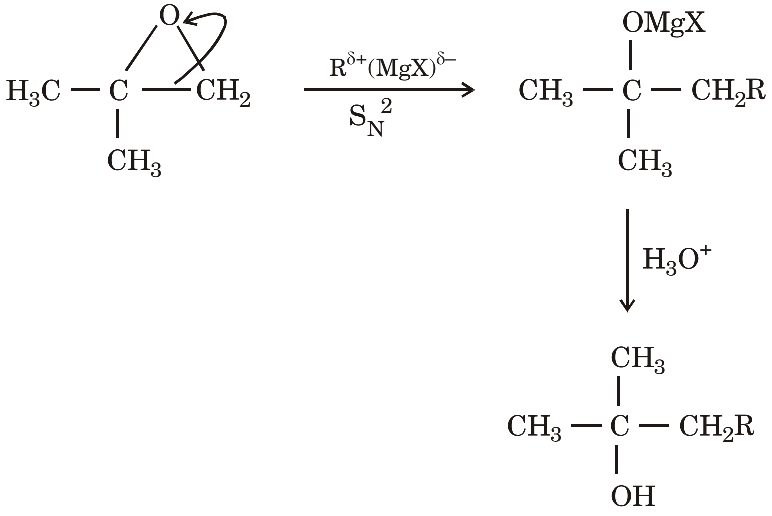
(1) Sterically hindered t-alcohols cannot be prepared by grignard reagent, but can be prepared using lithium alkyls. This is because lithium compounds are usually more reactive and yield a better product.



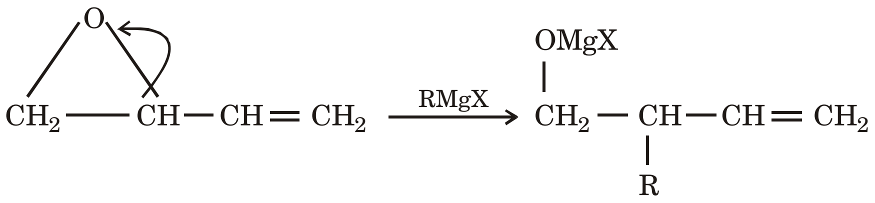
(2) For compounds like  $\underset{OH}{CH_2}-\underset{Cl}{CH_2}$, the reaction is :



(3) Reaction of RMgX with epoxide ring



(4)



{1 alcohol will be formed because of the allylic nature of 2 carbon}

3.2 By reduction

The chemical reducing agents like Lithium aluminium hydride ($LiAlH_4$), H_2/Ni, B_2H_6/THF etc. are used to produce alcohols.

(i) $LiAlH_4$

(a) $R - CHO \xrightarrow{LiAlH_4} -R - CH_2OH$

(b) $>C = O \xrightarrow{LiAlH_4} >CH - OH$

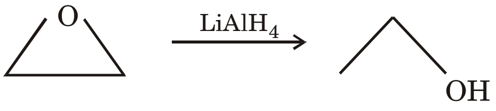
(c) $R - COOH \xrightarrow{LiAlH_4} R - CH_2OH$

(d) $R' - COOR \xrightarrow{LiAlH_4} R' - CH_2 - OH - + ROH$

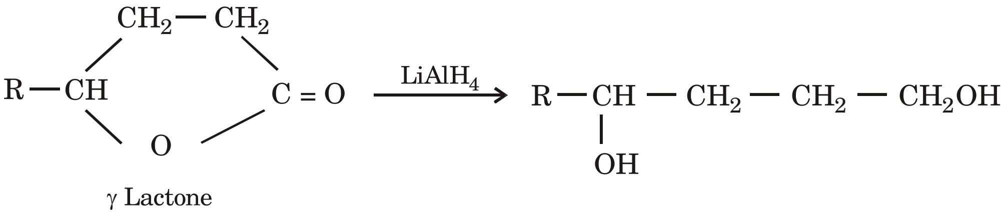
(e) $R - COCl \xrightarrow{LiAlH_4} R - CH_2 - OH$

(f) $(RCO)_2O \xrightarrow{LiAlH_4} R\,CH_2 - OH$

(g)



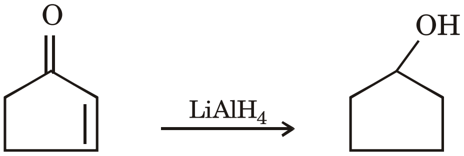
(h)



Note : $LiAlH_4$ does not reduce double or triple bonds however if double or triple bonds is in conjugation with (C = O) group, then double or triple bond is also reduced.

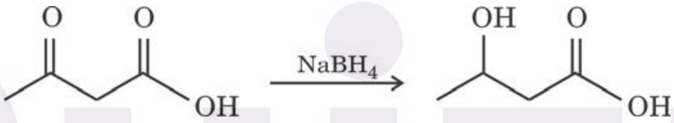
$$CH_2 = CH - CH_2 - CHO \xrightarrow{LiAlH_4} CH_2 = CH - CH_2 - CH_2OH$$

$$Ph - CH = CH - CHO \xrightarrow{LiAlH_4} Ph - CH_2 - CH_2 - CH_2OH$$



(ii) Using $NaBH_4$

It can reduce all the groups which are reduced by $LiAlH_4$ but cannot reduce carboxylic acid and ester. It can also reduce only the double bond which are in conjugation with C = O group.



(iii) By H_2/Ni

It can reduce all the groups reduced by $LiAlH_4$ and it can also reduce double and triple bonds in the carbonyl compounds irrespective of the position.

$$CH_3 - CH = CH - CHO \xrightarrow{H_2/Ni} CH_3 - CH_2\ CH_2\ CH_2 - OH$$

$$CH_2 = CH - CH_2 - CHO \xrightarrow{H_2/Ni} CH_3\ \ CH_2\ CH_2\ CH_2 - OH$$

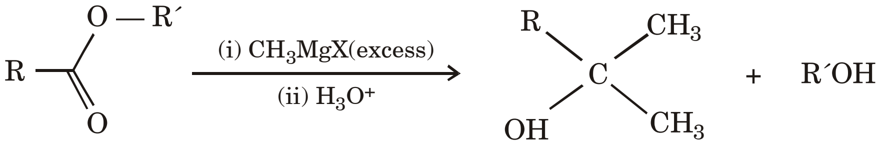
Note : Hydrogenolysis (cleavage by hydrogen) of an ester requires more severe conditions than simple hydrogenation of (addition of hydrogen to) a carbon-carbon double bond. High pressure and elevated temperatures are required : the catalyst used most often is a mixture of oxides known as copper chromite, of approximately the composition CuO. $CuCr_2O_4$. For example

$$\underset{\text{(Methyl dodecanoate)}}{CH_3\,(CH_2)_{10}\,COOCH_3} \xrightarrow[150°,\ 5000\,lb/in^2]{H_2,\ CuO\ CuCr_2O_4} \underset{\text{(1–Dodecanol)}}{CH_3\,(CH_2)_{10}\,CH_2\,OH} + CH_3\,OH$$

Chemical reduction is carried out by use of sodium metal and alcohol, or more usually by use of lithium aluminium hydride. For example

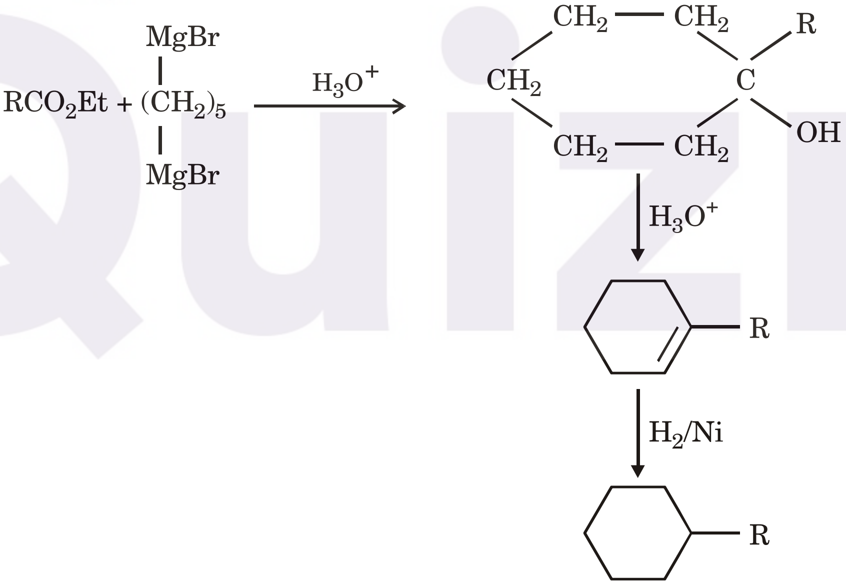
$$\underset{\text{(Ethyl hexadecanoate)}}{CH_3\,(CH_2)_{14}\,COOC_2H_5} \xrightarrow{LiAlH_4} \underset{\text{1–Hexadecanol}}{CH_3\,(CH_2)_{14}\,CH_2\,OH}$$

We have learnt that one molecule of an ester on reaction with excess of Grignard reagent followed by acidification produces a tertiary alcohol.



This simple reaction has a beautiful application in synthesis of cyclic tertiary alcohols, from which alicyclic hydrocarbons can be synthesized.

For Example :



Example 4

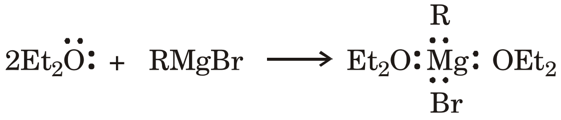
(a) **Why are ethers such as Et_2O used as solvents for (i) BF_3 and (ii) RMgBr ?**

(b) **Compare the Lewis basicities of tetrahydrofuran, diethyl ether and di–isopropyl ether and give your reasoning.**

Solution :

(a) Because of their unshared e⁻´s, there are also Lewis bases capable of reacting with Lewis acids such as BF_3 and RMgBr to form coordinate covalent bonds.

(i) $Et_2\ddot{O}\!: + BF_3 \longrightarrow Et_2\overset{+}{\ddot{O}}\!:\overset{-}{B}F_3$

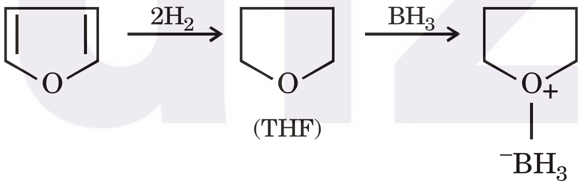
(ii) 

$2Et_2\ddot{O}\!: + RMgBr \longrightarrow Et_2O\!:\overset{R}{\underset{Br}{Mg}}\!: OEt_2$

Note that two molecules of ether coordinate tetrahedrally with one Mg^{2+}.

(b) In addition to the amount of electron density on the nucleophilic site, steric affects also influence basicities.The greater the steric hindrance encountered in the formation of the coordinate bond, the weaker is the Lewis basicity. In tetrahydrofuan, the R groups (the sides of the ring) are "tied back" leaving a very exposed O atom free to serve as a basic site. The 2 R groups in di–isopropyl ether furnish more steric hindrance than do the 1 ethyl groups in ethyl ether. The order of decreasing Lewis basicity in thus tetrahydrofuran > ethyl ether > i–propyl ether.

(iv) By **B_2H_6/THF**



This reduces all the groups reduced by LiAlH4 except acid chloride (–COCl). It does reduce the double / Triple bond but Selectively.

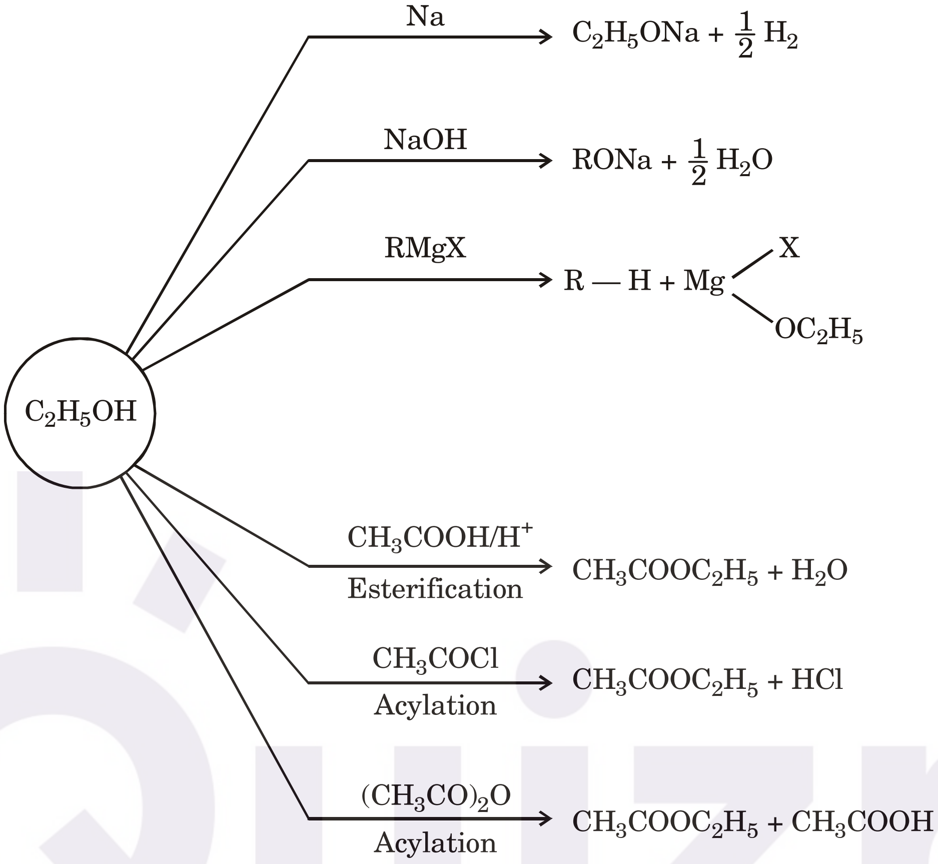
---

4. CHEMICAL PROPERTIES OF ALCOHOLS

In alcohols, –OH group is the functional group. The oxygen atom of –OH group polarize both the C – O bond and the O–H bond of any alcohol. Hence, alcohols can be classified into three types :

1. Reactions involving the cleavage of oxygen hydrogen bond.
2. Reactions involving the cleavage of carbon-oxygen bond.
3. Reactions involving both the alkyl and the hydroxyl groups.

I. Reactions involving cleavage of oxygen-hydrogen bond.



(i) The first three reactions illustrate the reactions of alcohols as acids.

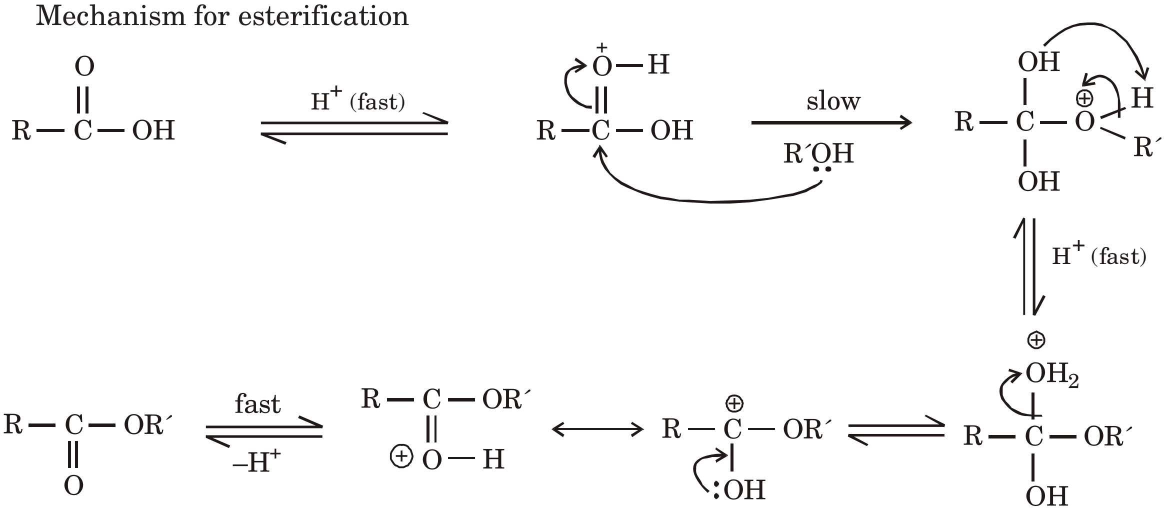
- **the order of acidic strength** of different types of alcohol is

$$\mathbf{CH_3OH > 1 > 2 > 3}$$

- the order of acidity for some compounds

$$\mathbf{H_2O > ROH > HC = CH > NH > RH}$$

(ii) Mechanism for esterification



(iii) **Acylation :** In this reaction, R – OH should be 1 or 2 .

Mechanism :

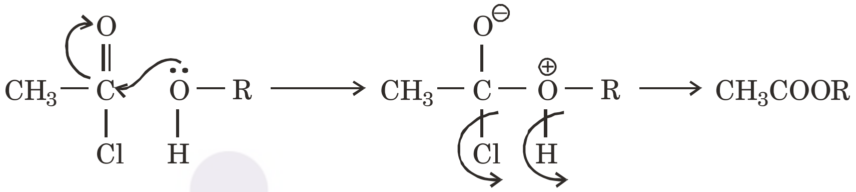
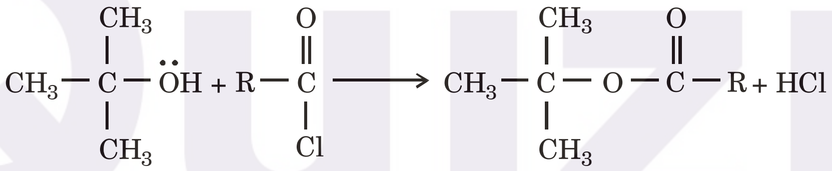
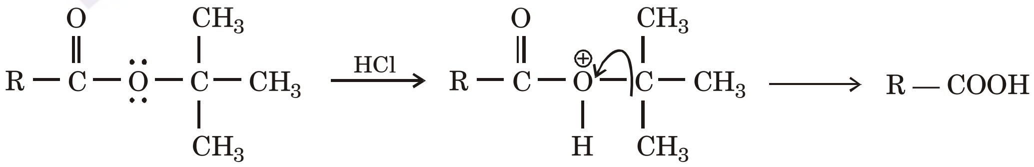


Illustration :

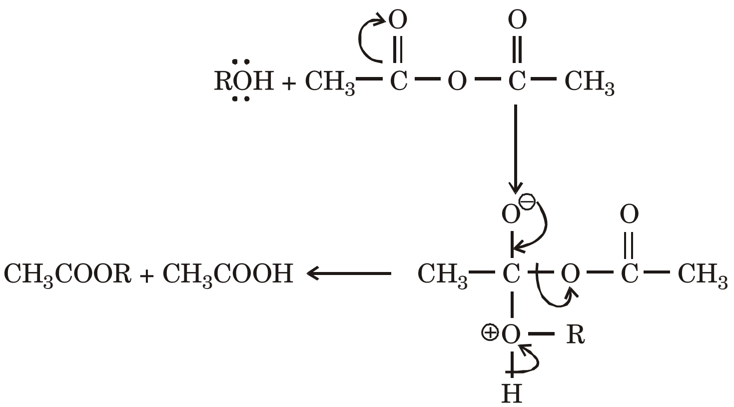


$$(CH_3)_3C-\ddot{O}H + R-\overset{O}{\overset{\|}{C}}-Cl \longrightarrow (CH_3)_3C-O-\overset{O}{\overset{\|}{C}}-R + HCl$$

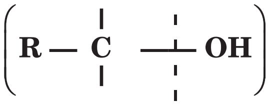
So, HCl formed above again attacks the oxygen atom.



(iv)

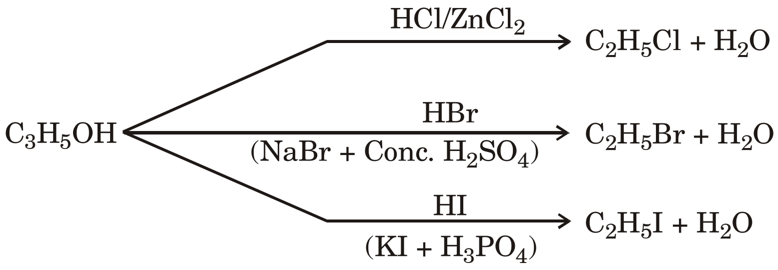


II. Reactions involving cleavage of carbon-oxygen Bond



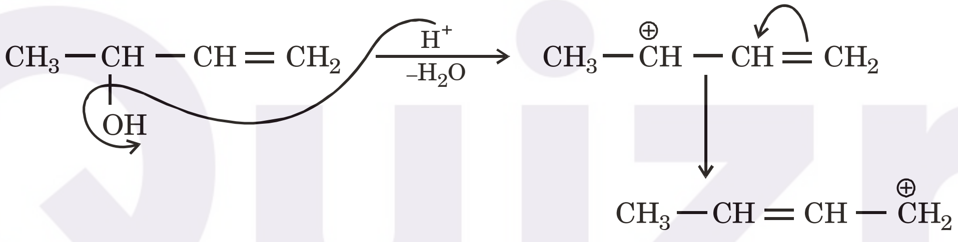
$\left(R-\overset{|}{\underset{|}{C}}\;\vdots\;OH\right)$

1. Reaction with hydrogen halide

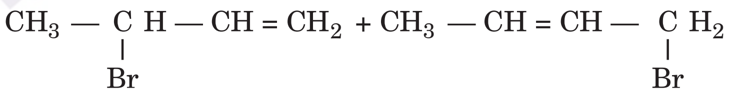


The order of reactivity of various halogen acids is **HI > HBr > HCl**

Illustration :



Hence, product formed is a mixutre of



$$CH_3-\underset{Br}{\underset{|}{C}}H-CH=CH_2 + CH_3-CH=CH-\underset{Br}{\underset{|}{C}}H_2$$

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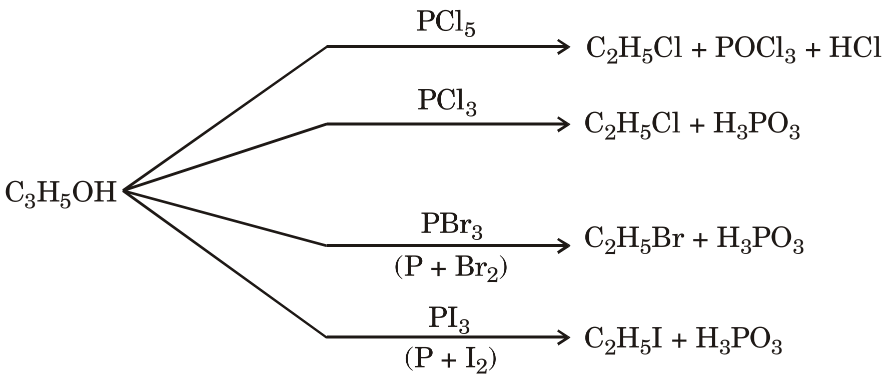
2. Reaction with phosphorus halides



3. Reactions with Thionyl Chloride

$$ROH + \underset{\substack{\text{Thionyl}\\ \text{chloride}}}{SOCl_2} \xrightarrow{\text{Pyridine}} RCl + SO_2\uparrow + HCl\uparrow$$

The order of reactivity is 3 > 2 > 1 . The reaction in presence of pyridine shows **inverted configuration**, while in absence of pyridine, it proceeds via S_Ni mehcanism showing **retention of configuration**.

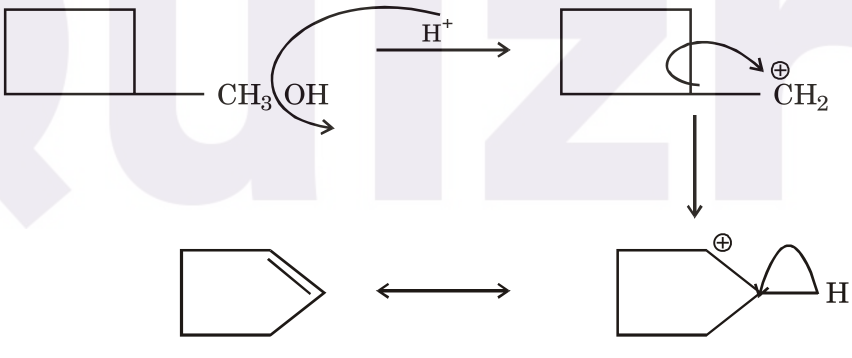
III. Reactions involving alkyl group as well as hydroxyl group

1. Acidic Dehydration

$$CH_3\ CH_2\ OH \xrightarrow{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

$$CH_3\ CH_2\ OH \xrightarrow{Al_2O_3} CH_2 = CH_2 + H_2O$$

The above reaction with conc. H_2SO_4 proceeds by E_1 mechanism. Hence, for



Stability of Rings 6 > 7, 5 > 8, 9 > > 4 > 3

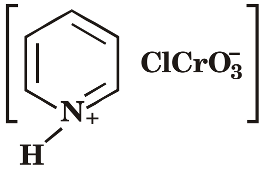
The ease of dehydration is 3 > 2 > 1

2. Oxidation

Alcohols undergo oxidation with oxidizing agents (in neutral or acidic or alkaline medium) such as CrO_3, $K_2Cr_2O_7$, KMO_4 or HNO_3.

(i) **PCC {Mixture of pyridine, HCl and CrO_3}**

Pyridinium Chloro Chromate



This reagent is used for **'controlled oxidation'**. It oxidizes 1 alcohols to aldehydes, but cannot convert them to carboxylic acids.

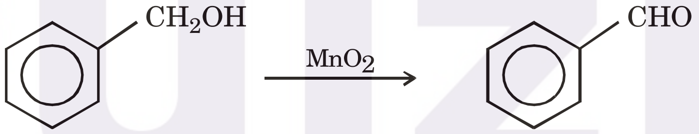
$$— CH_2OH \xrightarrow{P.C.C.} — CHO$$

$$R_2CHOH \xrightarrow{P.C.C.} — R_2CO$$

It is a mild oxidizing agent

$$3° \text{ alcohol} \xrightarrow{P.C.C.} \text{No reaction}$$

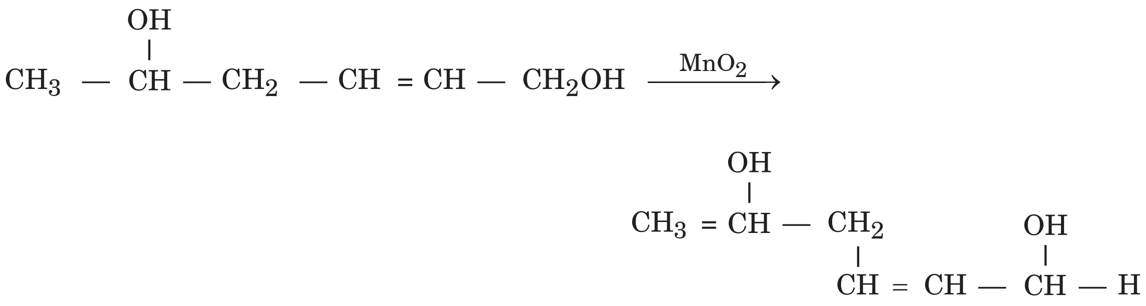
(ii) **MnO_2 :** It can selectively oxidise 1 allylic or 1 benzylic alcohols into aldehydes.



$$CH_2 = CH — CH_2OH \xrightarrow{MnO_2} CH_2 = CH — CHO$$

It does not oxidize or rearrange the double bonds.

Example :

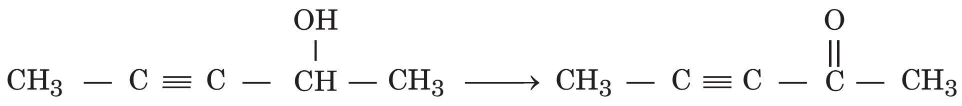


$$CH_3 — \overset{OH}{\overset{|}{CH}} — CH_2 — CH = CH — CH_2OH \xrightarrow{MnO_2}$$

$$CH_3 = \overset{OH}{\overset{|}{CH}} — \underset{CH = CH — \overset{OH}{\overset{|}{CH}} — H}{\underset{|}{CH_2}}$$

(iii) **H_2CrO_4 (Jones Reagent)**

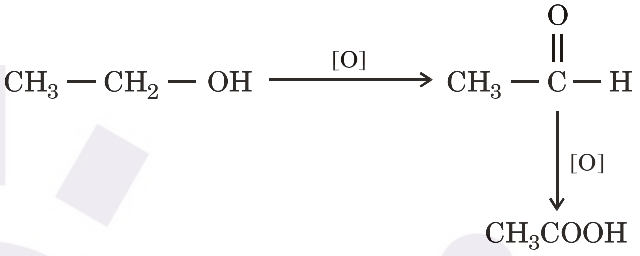
This reagent in presence of sulphuric acid is used for oxidation of alcohols. This is more oxidizing as compared to the above reagents, hence 2 alcohols react to form ketones. However, it does not oxidize double or triple bonds.



$$CH_3-C\equiv C-\overset{\displaystyle OH}{\overset{|}{C}H}-CH_3 \longrightarrow CH_3-C\equiv C-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

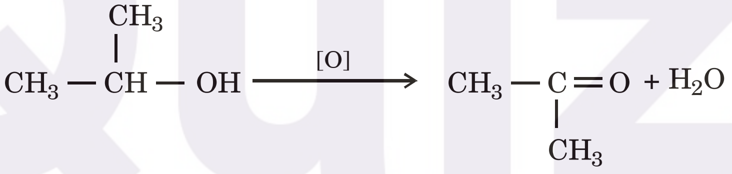
(iv) **$K_2Cr_2O_7$ or $KMnO_4$ or HNO_3** are strong oxidizing agents and directly oxidize 1 alcohols to carboxylic acids.

(a)



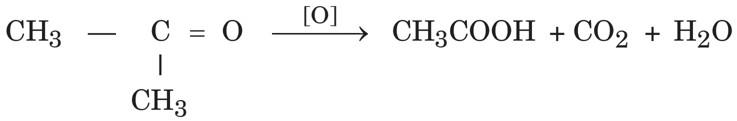
$$CH_3-CH_2-OH \xrightarrow{[O]} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow{[O]} CH_3COOH$$

(b)



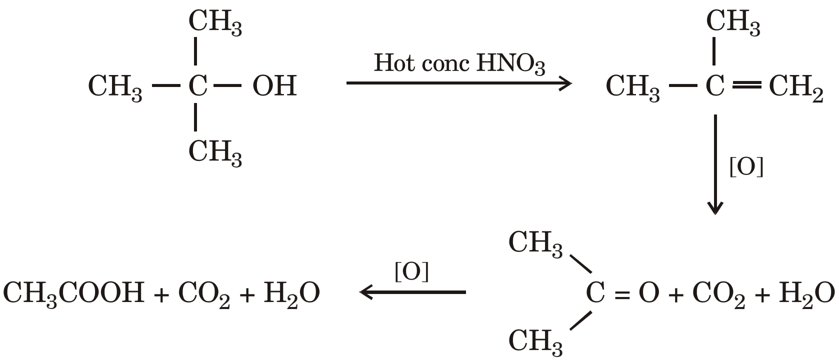
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-OH \xrightarrow{[O]} CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}O + H_2O$$

{under prolonged treatment with oxidizing agent, they get oxidized to acids with lesser number of carbon atoms than the alcohol}



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}=O \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$$

(c) 3 alcohols are not oxidised with mild oxidizing agents in aqueous, alkaline or under neutral conditions. However, when oxidation is carried out under acidic conditions, tertiary alcohols first undergo dehydration to alkene. The alcohol formed is then oxidized to ketone which is finally oxidized to carboxylic acid with lesser number of carbon atoms that the starting alcohol.

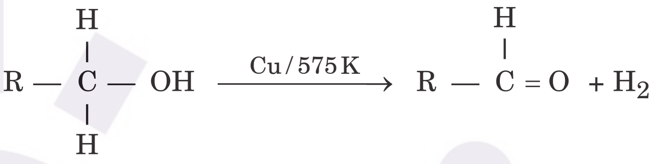


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow{\text{Hot conc } HNO_3} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow{[O]} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=O + CO_2 + H_2O \xrightarrow{[O]} CH_3COOH + CO_2 + H_2O$$

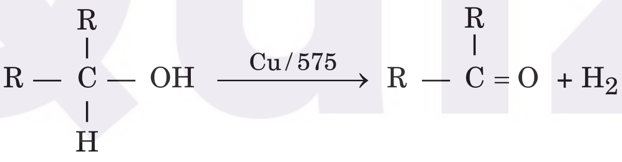
3. Dehydrogenation (Reduced with hot reduced copper)

(i) 1 alcohol.



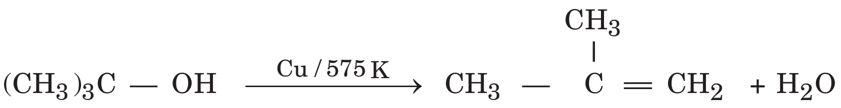
$$R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-OH \xrightarrow{Cu/575\,K} R-\overset{\overset{H}{|}}{C}=O + H_2$$

(ii) 2 alcohol



$$R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-OH \xrightarrow{Cu/575} R-\overset{\overset{R}{|}}{C}=O + H_2$$

(iii) 3 alcohol



$$(CH_3)_3C-OH \xrightarrow{Cu/575\,K} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 + H_2O$$

Note: The reagent can also be given a name of **'red hot copper tube'** in the question. However, it is the same as we have used above.

Example 5

Give the product of each reaction

(a) $CH_3CH_2CH = CHCH_2OH + MnO_2$

(b) $m—O_2NC_6H_4CH_2COOH + LiAlH_4$

(c) $Ph_2C = CHCH_3 + BH_3$, **THF followed by** H_2O_2/OH^-

(d) $PhCOCH_2CH_2Br + LiAlD_4$, **followed by** H_2O

(e) $PhCH = CHCH(OH)\ CH_3 + PBr_3/\Delta$

Solution :

(a) $CH_3CH_2CH = CHCHO$

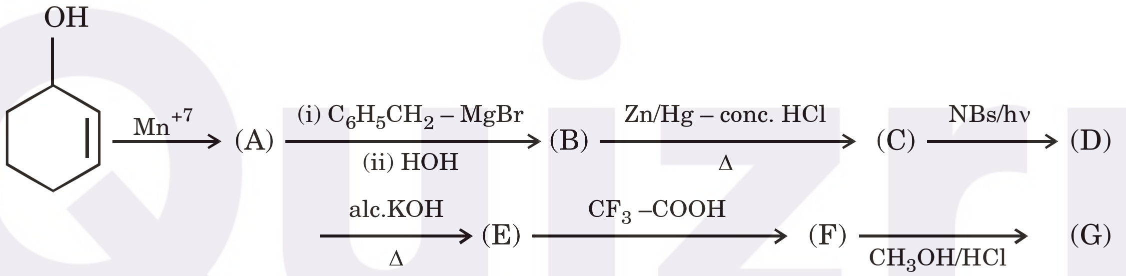
(b) $m–H_2NC_6H_4CH_2CH_2OH$

(c) $Ph_2CHCH(OH)CH_3$

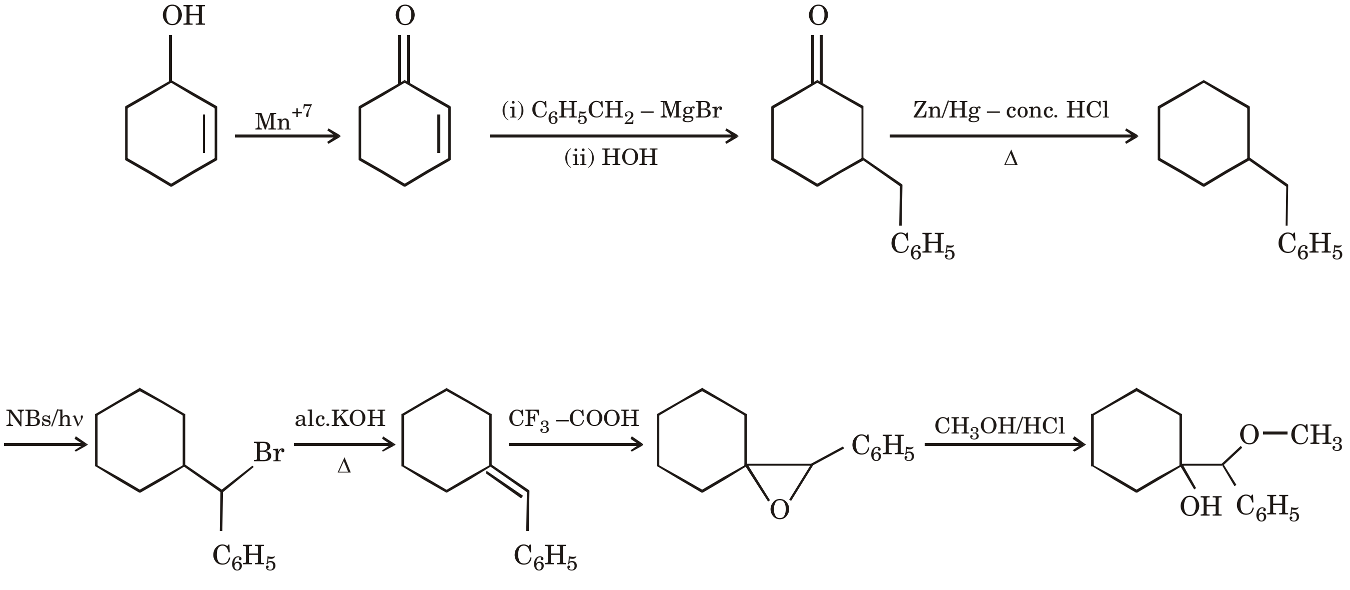
(d) $PhCD(OH)CH_2CH_2D$

(e) $PhCH = CHCHBrCH_3$

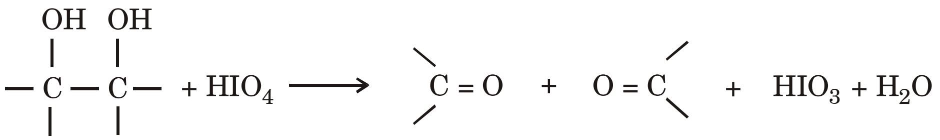
Example 6



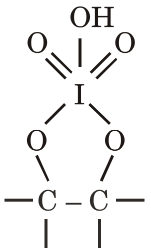
Solution :



Oxidative Cleavage of Diols



Reaction type : Oxidation-reduction



- 1, 2- or vicinal diols are cleaved by periodic acid, HIO_4, into two carbonyl compounds.
- The reaction is selective for 1, 2-diols.
- The reaction occurs via the formation of a cyclic periodate ester
- This can be used as a functional group test for 1, 2-diols.
- The products are determined by the substituents on the diol.

Example 7

Identify, each of the following glucose derivative

$$A + 5HIO_4 \longrightarrow 4HCOOH + 2HCHO$$

$$B + 3HIO_4 \longrightarrow 2HCOOH + 2OHC - COOH$$

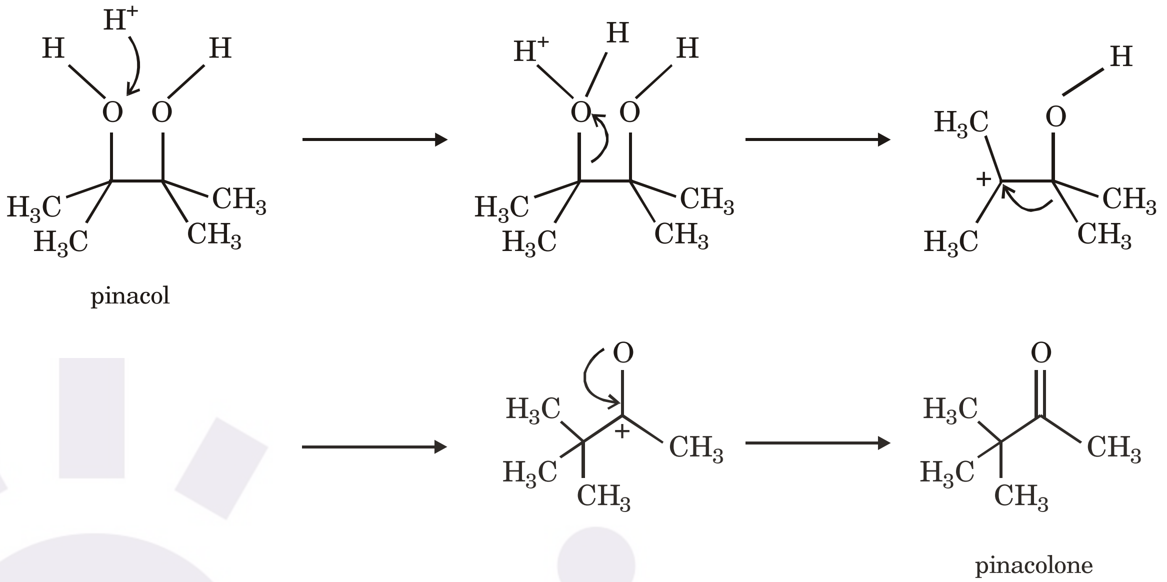
Solution :

A → $HOCH_2CH(OH)CH(OH)CH(OH)CH(OH).CH_2OH$

B → HOOC.CH(OH) . CH(OH) . CH(OH) . CH(OH) . COOH

PINACOL REARRANGEMENT

The pinacol rearrangement or pinacol-pinacolone rearrangement is a method for converting a 1, 2-diol to a carbonyl compound. This rearrangement takes place under acidic conditions. The name of the reaction comes from the rearrangement of pinacol to pinacolone.



An overview of mechanism

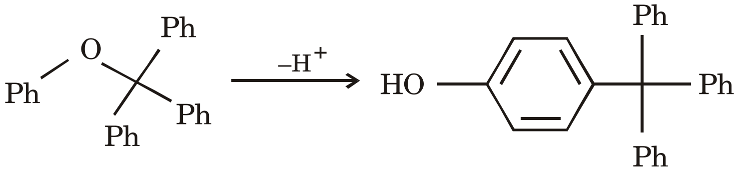
Protonation of one of the –OH groups occurs and a carbocation is formed. If both the –OH groups are not alike, then the one which yields a more stable carbocation participates in the reaction. Subsequently, an alkyl group from the adjacent carbon migrates to the carbocation center. The driving force for this rearrangement step is believed to be the relative stability of the resultant oxonium ion, which has complete octet configuration at all centers (as opposed to the preceding carbocation). The migration of alkyl groups in this reaction occurs in accordance with their usual migratory aptitude, i.e. Ph- > 3-alkyl > 2-alkyl > 1-alkyl > H.

Stereochemistry of the rearrangement

In cyclic systems, the reaction presents more features of interest. In these reactions, the stereochemistry of the diol plays a crucial role in deciding the major product.

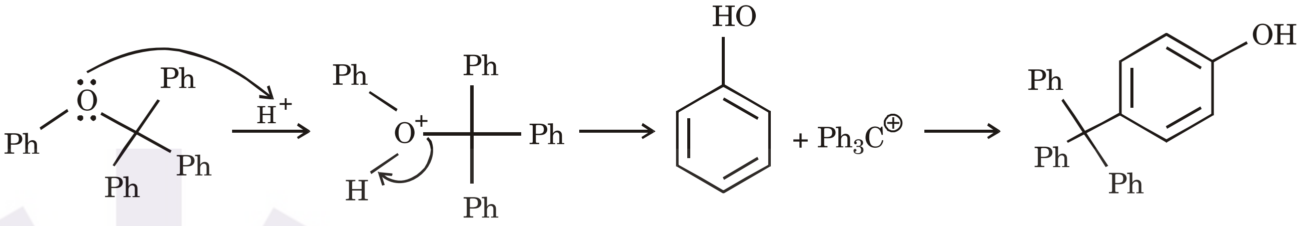
- An alkyl group which is situated trans-to the leaving –OH group alone may migrate. If otherwise, ring expansion occurs, i.e. the ring carbon itself migrates to the carbocation centre.
- If the migrating alkyl group has a chiral center as its key atom, the configuration at this center is retained even after migration takes place.

Exampl 8



Explain the mechanism.

Solution :

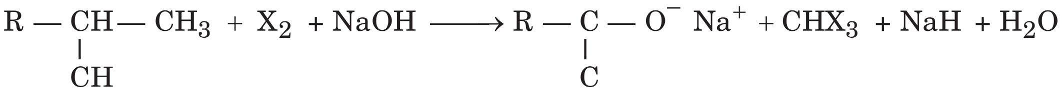


> **NOTE : A number of experiments have been carried out to determine the relative migratory aptitude of -groups in Pinacol/Pinacolone type rearrangement.**
>
> **$H > Ph > Me_3C > MeCH_2 > Me$**

DISTINCTION BETWEEN 1°, 2°, 3° ALCOHOLS

1. Haloform Reaction

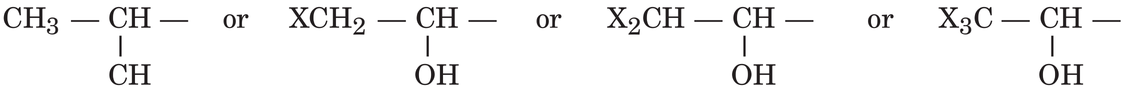
The general reaction is represented as



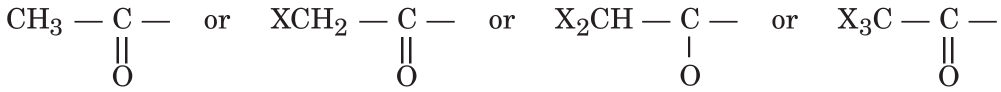
$$R-\underset{\underset{CH}{|}}{CH}-CH_3+X_2+NaOH\longrightarrow R-\underset{\underset{C}{|}}{C}-O^-\ Na^++CHX_3+NaH+H_2O$$

The CH_3 carbon is lost as CHX_3 and the remaining part exists as acid salt, which can be acidified to liberate free acid.

The structural feature essential in the compound to show haloform reaction is that any of the following moieties should be present in the molecule attached to some electron-withdrawing group or electron donating group by +I only.



$$CH_3-\underset{\underset{CH}{|}}{CH}-\quad\text{or}\quad XCH_2-\underset{\underset{OH}{|}}{CH}-\quad\text{or}\quad X_2CH-\underset{\underset{OH}{|}}{CH}-\quad\text{or}\quad X_3C-\underset{\underset{OH}{|}}{CH}-$$



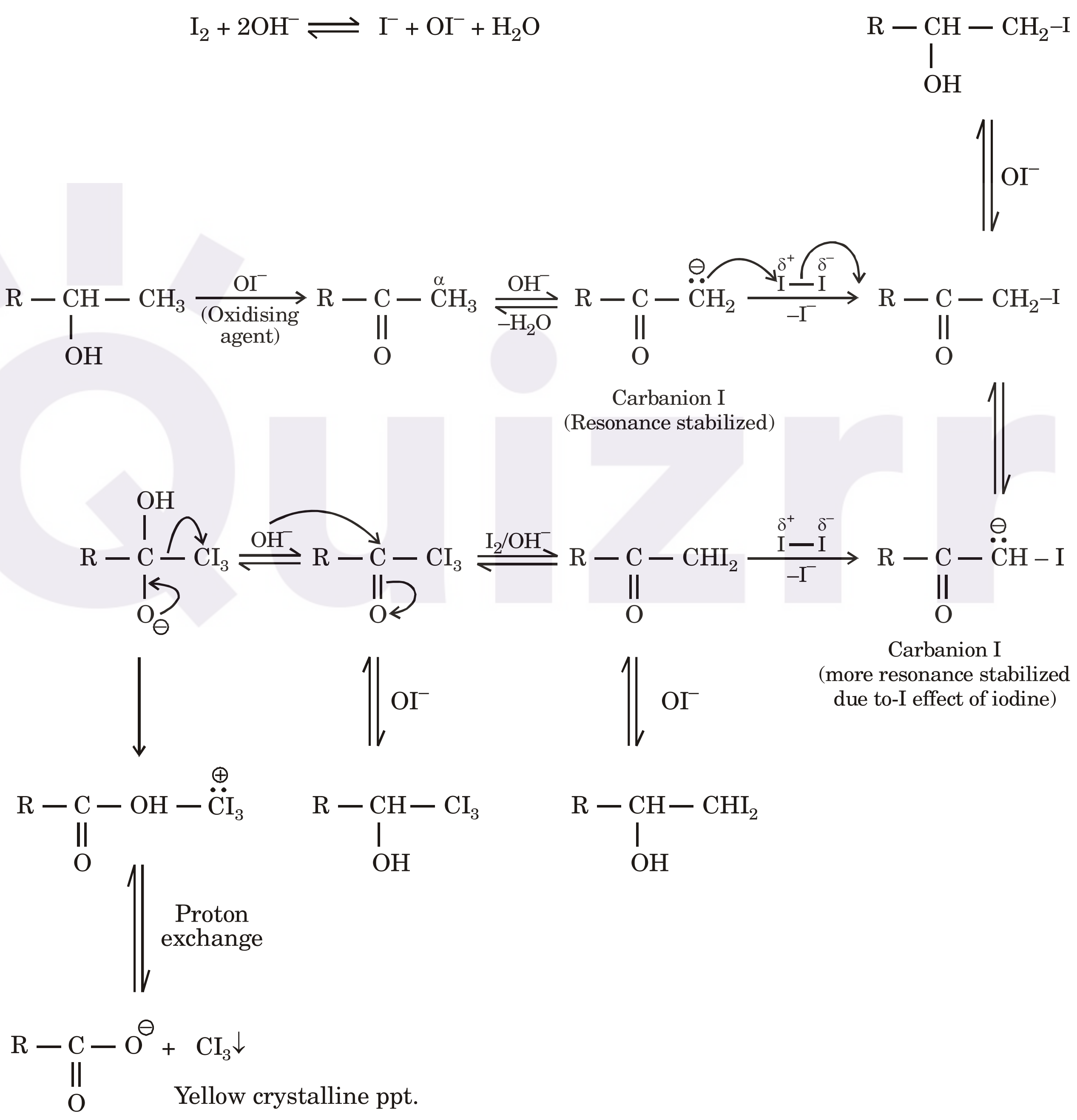
$CH_3-\underset{\underset{O}{\|}}{C}-$ or $XCH_2-\underset{\underset{O}{\|}}{C}-$ or $X_2CH-\underset{\underset{O}{|}}{C}-$ or $X_3C-\underset{\underset{O}{\|}}{C}-$

or any other grouping that can be converted to any of the above moieties.

The mechanism of the reaction can be outlined as :

The reaction has 3 important steps. Step I is the oxidation, caused by mild oxidizing agent (hypo halite ion). The second step is base-promoted halogenation and the third step is cleavage of C–C bond.

$I_2 + 2OH^- \rightleftharpoons I^- + OI^- + H_2O$



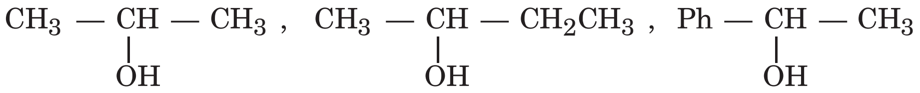
Carbanion I
(Resonance stabilized)

Carbanion I
(more resonance stabilized due to-I effect of iodine)

Yellow crystalline ppt.

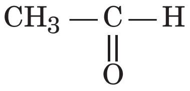
Some of the compounds which responds positively to iodoform test are

CH_3CH_2OH (only primary alcohol)



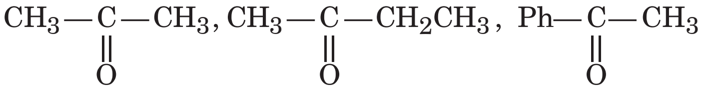
$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3,\ CH_3-\underset{OH}{\underset{|}{CH}}-CH_2CH_3,\ Ph-\underset{OH}{\underset{|}{CH}}-CH_3$$

(secondary alcohols)



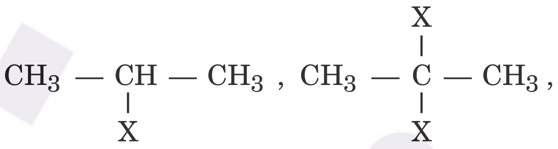
$$CH_3-\underset{O}{\underset{\|}{C}}-H$$

(only aldehyde)

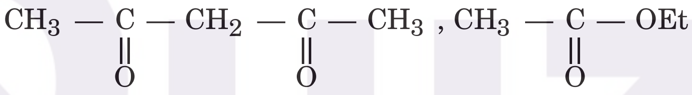


$$CH_3-\underset{O}{\underset{\|}{C}}-CH_3,\ CH_3-\underset{O}{\underset{\|}{C}}-CH_2CH_3,\ Ph-\underset{O}{\underset{\|}{C}}-CH_3$$

(ketones)

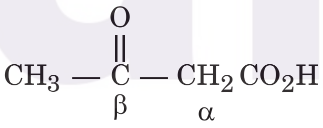


$$CH_3-\underset{X}{\underset{|}{CH}}-CH_3,\ CH_3-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-CH_3,$$



$$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-CH_3,\ CH_3-\underset{O}{\underset{\|}{C}}-OEt$$

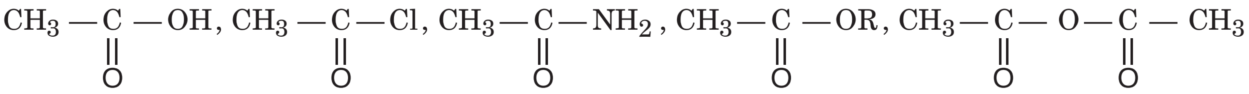
(after heating with OH–)



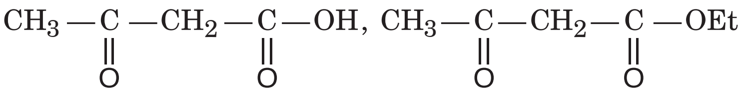
$$CH_3-\overset{O}{\overset{\|}{\underset{\beta}{C}}}-\underset{\alpha}{CH_2}CO_2H$$

(after heating)

The compounds that respond negatively to iodoform test are



$$CH_3-\underset{O}{\underset{\|}{C}}-OH,\ CH_3-\underset{O}{\underset{\|}{C}}-Cl,\ CH_3-\underset{O}{\underset{\|}{C}}-NH_2,\ CH_3-\underset{O}{\underset{\|}{C}}-OR,\ CH_3-\underset{O}{\underset{\|}{C}}-O-\underset{O}{\underset{\|}{C}}-CH_3$$

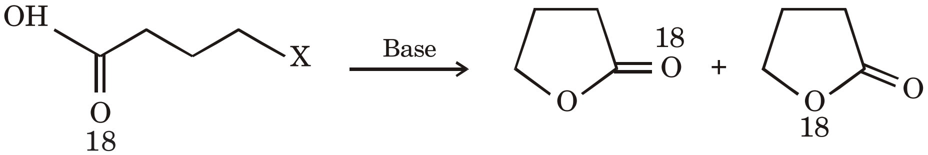


$$CH_3-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-OH,\ CH_3-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-OEt$$

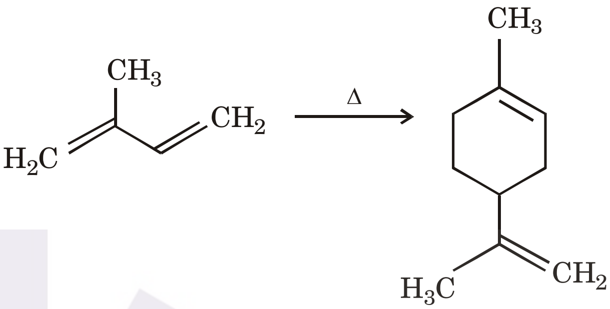
Example 9

Explain the following reactions with a proper mechanism.

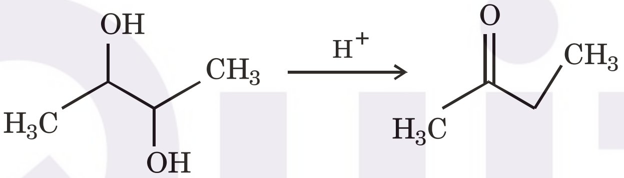
(a)



(b)

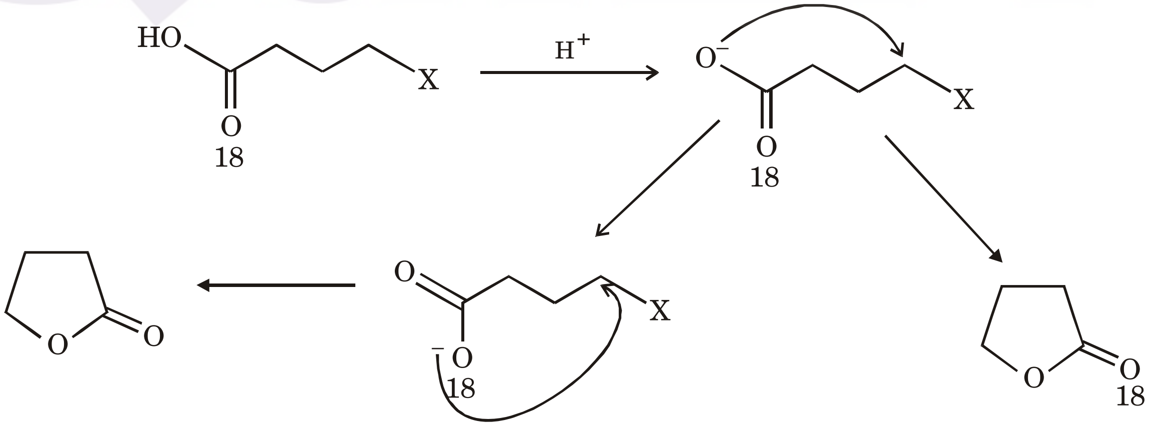


(c)

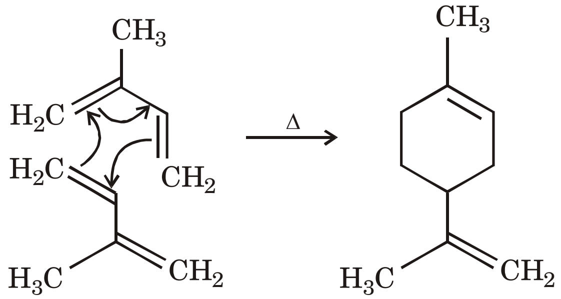


Solution :

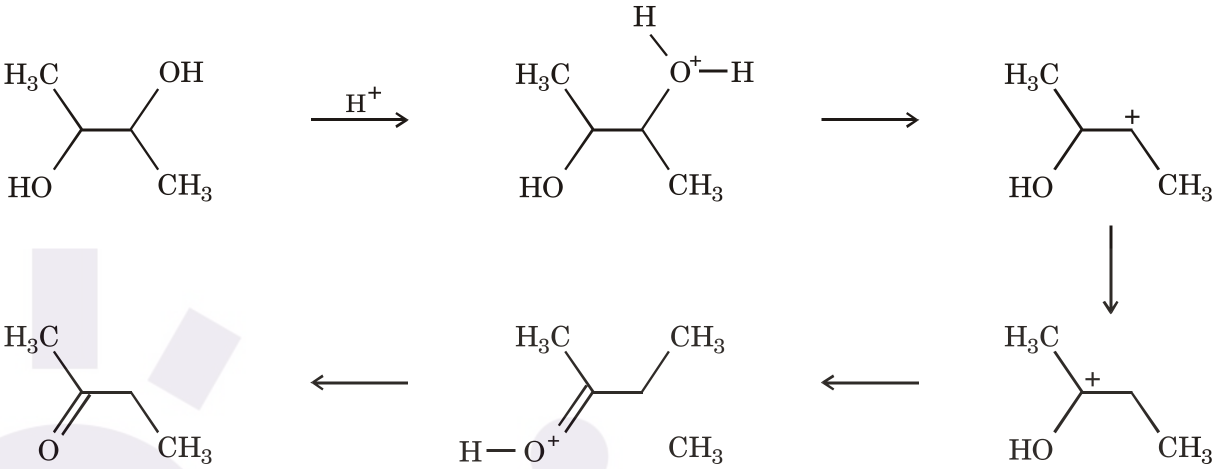
(a)



(b)



(c)



2. **Lucas Test**

Alcohols react with concentrated hydrochloric acid in the presence of anhydrous zinc chloride to form alkyl chlorides. The alkyl chlorides appear as cloudiness because of its insolubility in Lucas reagent.

$$R - OH + HCl \xrightarrow{ZnCl_2} \underset{\text{Alkyl halide}}{R - Cl + H_2O}$$

The three types of alcohols undergo this reaction at different rates. The rates of reaction with Lucas reagent [conc. HCl + $ZnCl_2$ (anhydrous)] follow the given order :

Tertiary alcohol > Secondary alcohol> Primary alcohol

An unknown alcohol (monohydric) is mixed with conc. HCl and anhydrous ZnCl2 at room temperature. The alkyl chloride formed is insoluble in the medium, thus the solution becomes cloudy before it separates out as a distinct layer. The following observations are made,

(a) If cloudiness (white turbidity) appears immediately, the alcohol is tertiary.

(b) If cloudiness appears within 5 minutes, the alcohol is secondary.

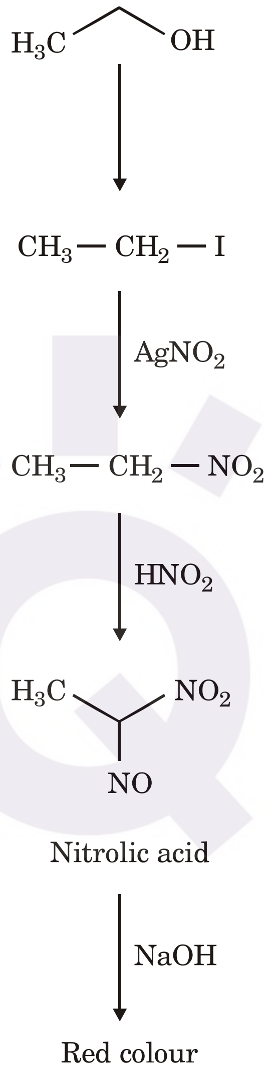
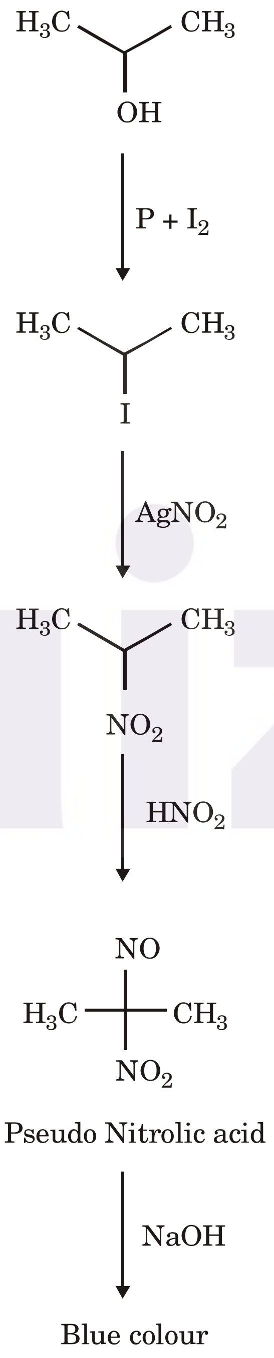
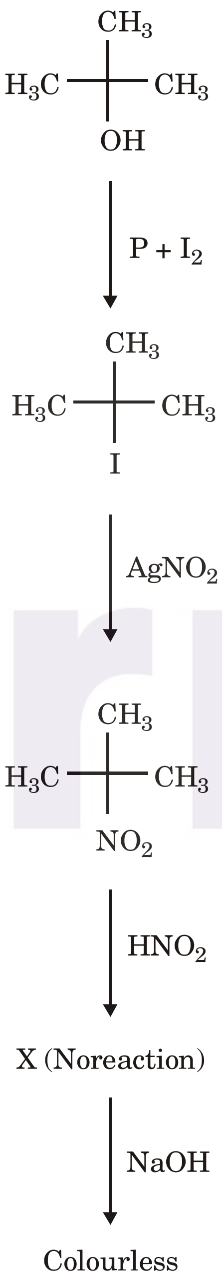
(c) If the solution remains clear, i.e., no cloudiness is formed the alcohol is primary.

Remember that the benzyl and allyl alcohol react as rapidly as tertiary alcohol with Lucas reagent because their cations are resonance stabilised and as stable as 3 carbocations.

3. Victor Mayer Test :

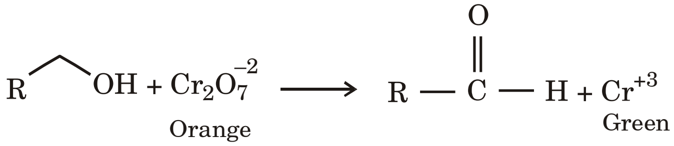
It follows in four stages :

(i) P + I_2, (ii) $AgNO_2$, (iii) HNO_2, (iv) Base

Primary alcohol	**Secondary Alcohol**	**Tertiary alcohol**
		

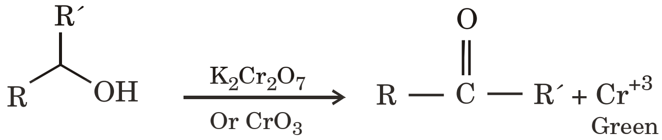
4. Oxidation Test

(i) Primary alcohol on oxidation in presence of acidic chromate gives aldehyde



Colour will charge from orange to green.

(ii) Secondary alcohols gives Ketones by chromic acid



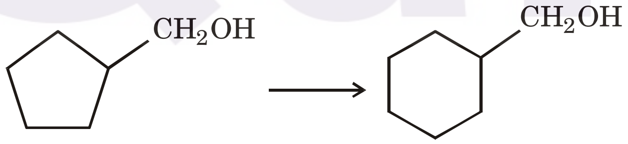
Here also colour will not change.

(iii) 3 alcohol don’t oxidise in alkaline condition but in acidic condition, it rapidly dehydrates to alkene. Colour doesn’t change.

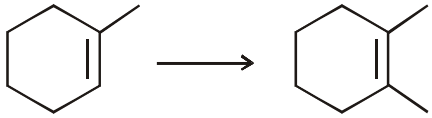
Exercise 10

Effect the following conversions.

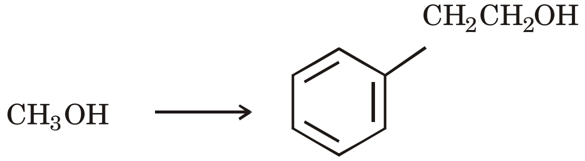
(a)



(b)

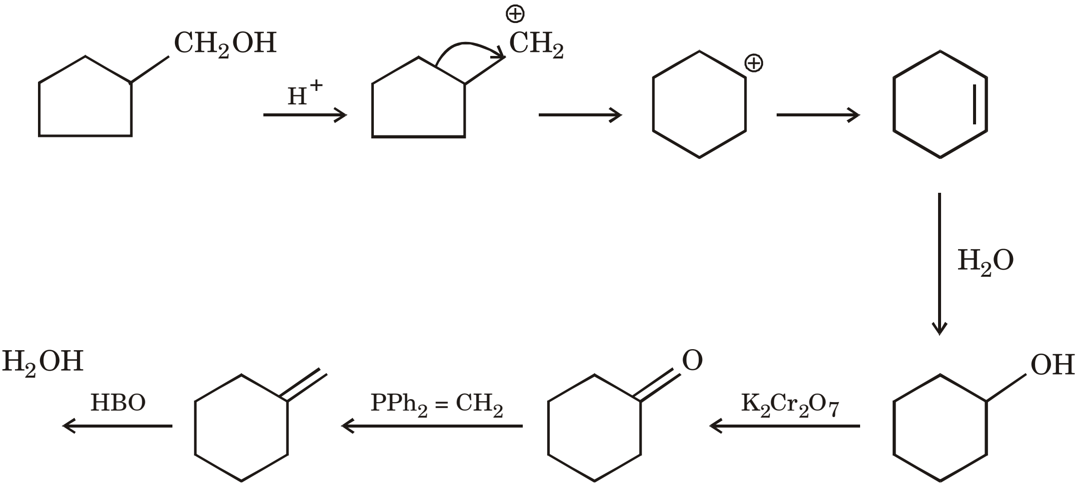


(c)

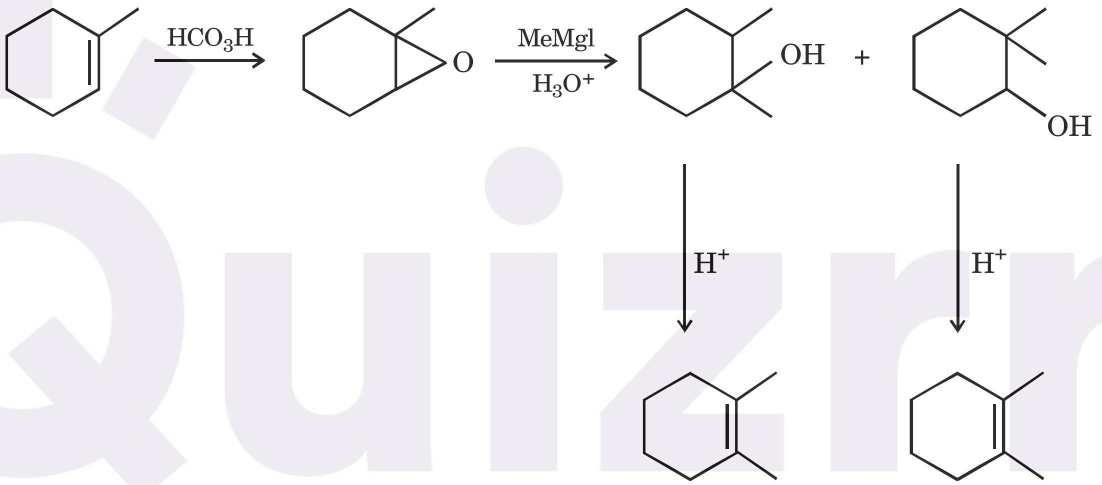


Solution :

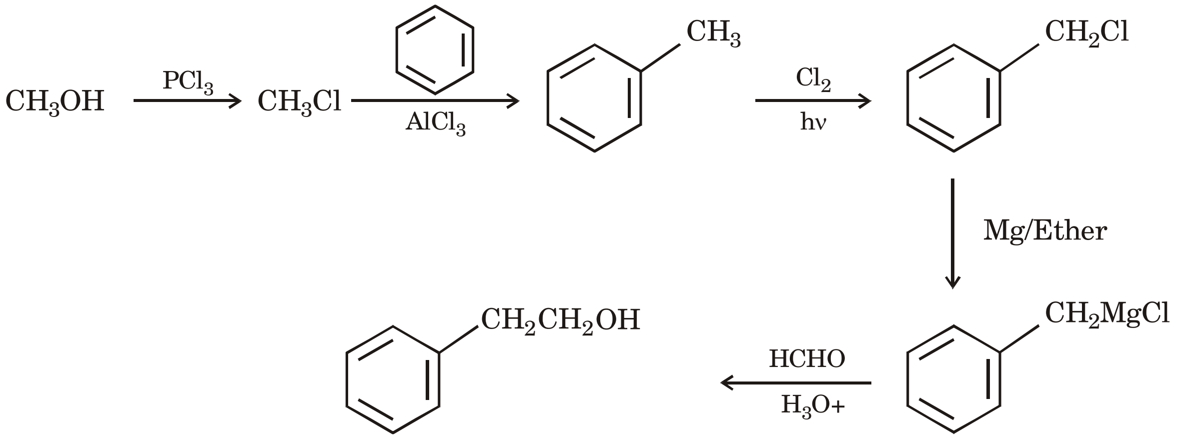
(a)



(b)



(c)



Exercise 11

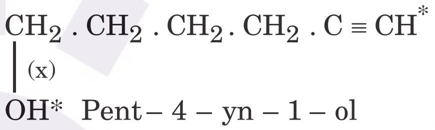
Compound (X) (C_5H_8O) does no react appreciably with Lucas reagent at room temperature but gives a precipitate with ammonical silver nitrate. With excess of MeMgBr, 0.42 g of (X) gives 224 ml CH_4 at STP. Treatment of (X) with H_2 in presence of Pt. catalyst followed by boiling with excess HI gives n-pentane. Suggest structure for (X) and write the equations involved.

Solution :

(1) (X), (C_5H_8O) does not react with Lucas reagent appreciably at room temperature but gives precipitate with ammonical $AgNO_3$ and thus, (X) has terminal alkyne linkage as well as primary alcoholic group.

(2) (X) on hydrogenation and then reacting with HI gives pentane and thus, (X) is straight chain compound.

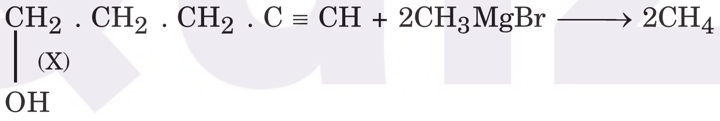
(3) Keeping in view of the above facts (X) may be



$$\underset{\underset{\text{OH}^*}{|\,(x)}}{\text{CH}_2}\,.\,\text{CH}_2\,.\,\text{CH}_2\,.\,\text{CH}_2\,.\,\text{C}\equiv\text{CH}^*$$

Pent – 4 – yn – 1 – ol

(4) Its reaction with MeMgBr gives CH_4. (It has two acidic or active H* atoms) and thus, 1 mole of (X) will give two mole of CH_4.



$$\underset{\underset{\text{OH}}{|\,(X)}}{\text{CH}_2}\,.\,\text{CH}_2\,.\,\text{CH}_2\,.\,\text{C}\equiv\text{CH} + 2\text{CH}_3\text{MgBr} \longrightarrow 2\text{CH}_4$$

∵ 84 g (X) gives 2   22.4 litre CH4

∵ 0.42 g (X) will give $\frac{2 \times 22.4 \times 0.42}{84}$ = **224 ml CH_4**

Given fact is confirmed.

Thiols

Nomenclature :

Thiols are the sulfur analogues of alcohols.

Functional group suffix = – thiol

Functional group prefix = mercapto

Physical Properties :

- Hydrogen bonding is much weaker than that in alcohols.
- Lower boiling points than similar alcohols.

Structure :

- Generally similar to alcohols, but bonds to S are longer and weaker than those to O.
- The thiol functional group consists of an S atom bonded to a C atom and a H atom via σ bonds.
- The S–H bonds is less polar than that in alcohols since S is less electronegativity than O.

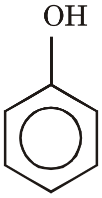
Reactivity :

- Thiols are much more acidic than similar alcohols, e.g., RSH (pKa = 10) versus ROH (pKa = 16 to 19)

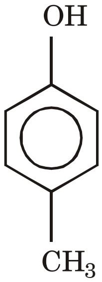
PHENOLS

When hydroxyl group is directly attached to the benzene ring, the compounds are called phenols.

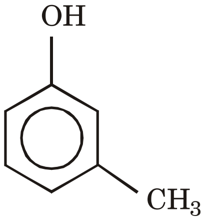
Some examples :



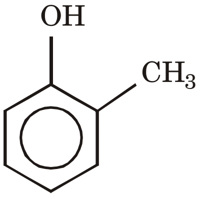
phenol



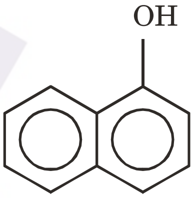
P-cresol



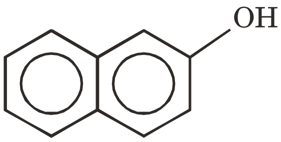
m-cresol



o-cresol



1-naphthol
(α-naphthol)



2-naphthol
(β-naphthol)

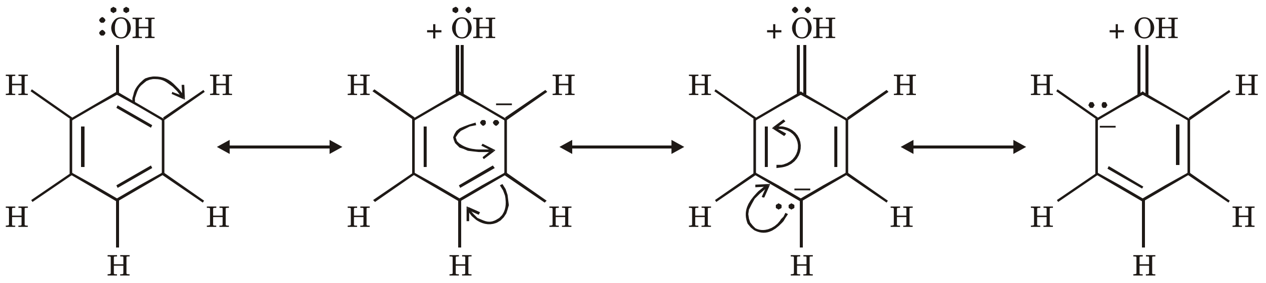
Physical Properties :

- The polar nature of the O–H bond (due to the electronegativity difference of the atoms) results in the formation of hydrogen bonds with other phenol molecules or other H-bonding systems (e.g. water). The implications of this are :
  * high melting and boiling points compared to analogous arenes
  * high solubility in aqueous media
- The presence of intramolecular hydrogen bonding is believed responsible for the significantly lower boiling points of certain ortho-substituted phenols vs the meta-and para-analogs.

Structure :

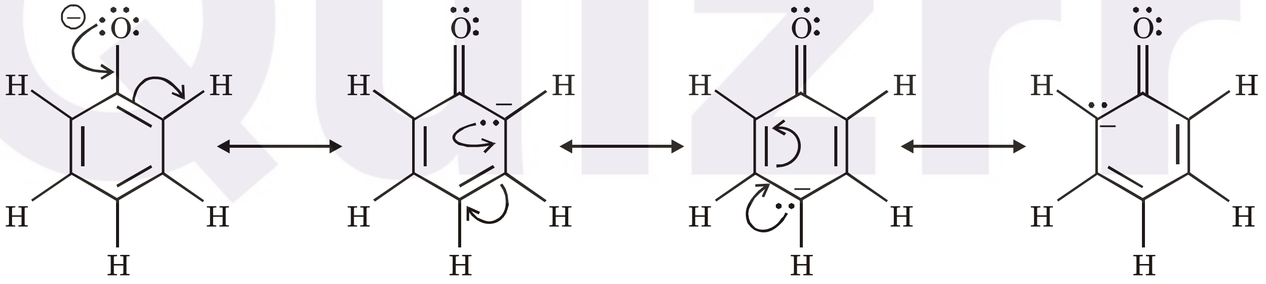
- The alcohol functional group consists of an O atom bonded to an sp^2–hybridised aromatic C atom and a H atom via σ bonds.
- Both ther C–O and the O–H bonds are polar due to the high electronegativity of the O atom.
- Conjugation exists between an unshared electron pair on the oxygen and the aromatic ring.

- This results in, compared to simple alcohols :
  - a shorter carbon-oxygen bond distance
  - a more basic hydroxyl oxygen
  - a more acidic hydroxyl proton (–OH)



Acidity

- Phenols are more acidic ($pK_a \approx 10$) than alcohols ($pK_a \approx 16 - 20$), but less acidic than carboxylic acids ($pK_a \approx 5$)
- The negative charge of the phenolate ion is stabilised by resonance due to electron delocalisation onto the ring as shown below :



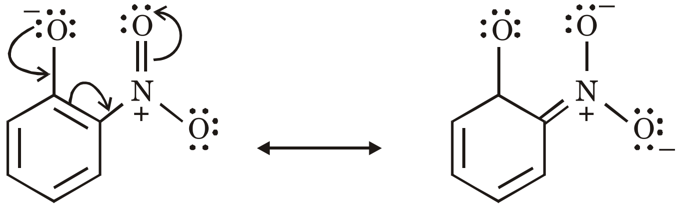
- The acidity difference means that it is possible to separate phenols from alcohols and/or carboxylic acids.

  * Mixing an ether solution, of either phenol and alcohol or phenol and carboxylic acid, with dilute base (sodium hydroxide and sodium bicarbonate, respectively), results in the stronger acid being converted to its alkali salt, which is then extracted to the aqueous phase and can be separated from the organic phase.

- Nucleophilic substitution reactions of phenols are generally carried out under basic conditions as the phenolate ion is a better nucleophile.

Substituent Effects on Acidity

Substituents, particularly those located ortho or para to the –OH group, can dramatically influence the acidity of the phenol due to resonance and / or inductive effects. Electron withdrawing groups enhance the acidity, electron donating substituents decrease the acidity. The resonance stabilisation of o-nitrophenol is shown below :



Acidity of Phenol can be explained by :

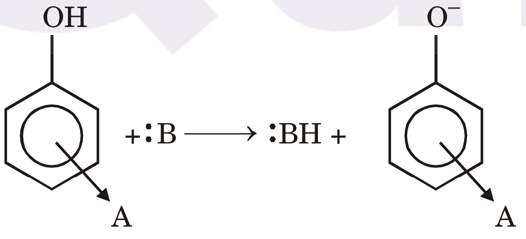
(a) electron – attracting and

(b) electron – releasing substituents on the acid strength of phenols are as follows.

Electron – attracting substituents disperse negative charges and therefore stabilize ArO$^-$ and increase acidity of ArOH. Electron – releasing substituents concentrate the negative charge on O destabilizes ArO$^-$ and decreases acidity of ArOH.

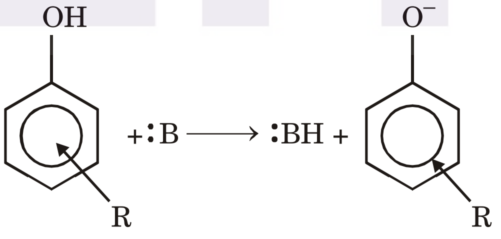
Electron – Attracting **Electron – Releasing**

(— NO_2, — CN, — CHO, — COOH, — NR_3, — X)



More acidic

Charge dispersed Ion stabilized



Less acidic

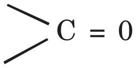
Charge concentrated Ion destabilized

I. In terms of resonance and inductive effects we can account for the following relative acidities.

(a) $p–O_2NC_6H_4OH > m–O_2C_6H_4OH > C_6H_5OH$

(b) $m–ClC_6H_4OH > p\text{-}ClC_6OH > C_6H_5OH$

(a) The – NO_2 is electron – withdrawing and acid – strengthening. Its resonance effect, which occurs only from para and ortho positions, predominates over its inductive effect, which occurs also from the meta position. Other substituents in this category are



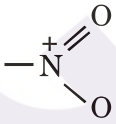
– CN –COOR –SO_2R

(b) Cl is electron – withdrawing by induction. This effect diminishes with increasing distance between Cl and OH. The meta is closer than the para positions and m-Cl is more acid – strengthening than the p-Cl. Other substituents in this category are F, Br, I, $^{+}NR_3$.

II. We can compare the relative acid strengths in the following groups :

(a) phenol, m-chlorophenol, m-nitrophenol, m-cresol;
(b) phenol, benzoic acid, p-nitrophenol, carbonic acid
(c) phenol, p-chlorophenol, p-nitrophenol, p-cresol
(d) phenol, o-nitrophenol, m-nitrophenol, p-cresol
(e) phenol, p-chlorophenol, 2, 4, 6 – trichlorophenol, 2, 4–dichlorophenol
(f) phenol, benzyl alcohol, benzenesulfonic acid, benzoic acid

(a)



Because NO_2 has + on N, it has a greater electron – withdrawing inductive effect than Cl.

The decreasing order of relative acid strengths

m-nitrophenol > m-chlorophenol > phenol > m-cresol

(b) The decreasing order of relative acid strengths

Benzoic acid > carbonic acid > p-nitrophenol > phenol

(c) The resonance effect of p–NO_2 exceeds the inductive effect of p–Cl p-CH_3 is electron releasing.

The decreasing order of relative acid strengths

p-nitrophenol > p-chlorophenol > phenol > p-cresol

(d) Intramolecular H-bonding makes the o-isomer weaker than the p-isomer.

The increasing order of relative acids strengths

p-nitrophenol > o-nitrophenol > m-nitrophenol > phenol

(e) The decreasing order of relative acids strengths

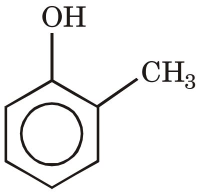
2, 4, 6–trichlorophenol > 2, 4,–dichlorophenol > p-chlorophenol > phenol

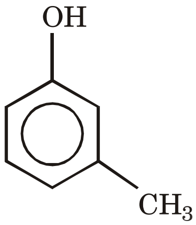
(f) The decreasing order of relative acid strengths

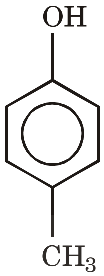
benzenesulfonicacid > benzoic acid > phenol > benzyl alcohol

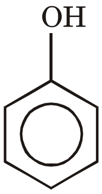
Example 12

Compare acidic order of


ortho


meta


para



Solution :

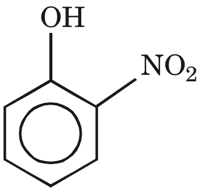
— CH_3 is electron donating group by inductive effect as well as resonance. Therefore ortho and para will be least acidic and phenol most. Among ortho & para, inductive effect is greater at ortho position, therefore it will be less acidic than para.

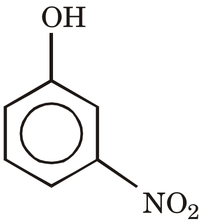
Therefore

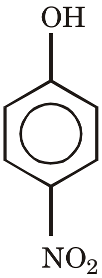
phenol > meta > para > ortho

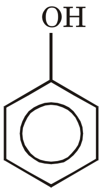
Example 13

Compare acidity of









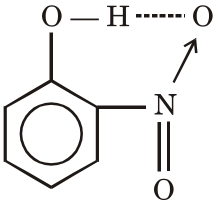
Solution :

NO_2 is e– withdrawing both by resonance.

Therefore order should be

ortho > para > meta > phenol

but its not the case due to H bonding at ortho position

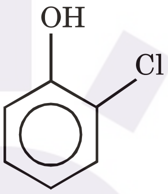


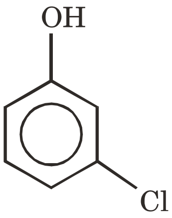
This correct order is

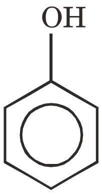
para > ortho > meta > phenol

Example 14

Compare acidity of







Solution :

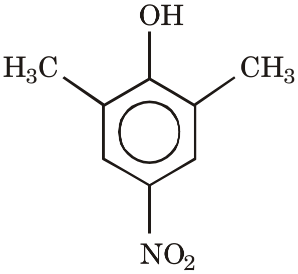
– Cl is e– withdrawing by inductive effect

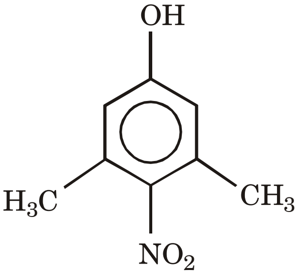
and e– donating by resonance & former dominates over later.

∴ o > m > p > ϕ

where o — ortho, m — meta, p — para, ϕ — phenol

Example 15

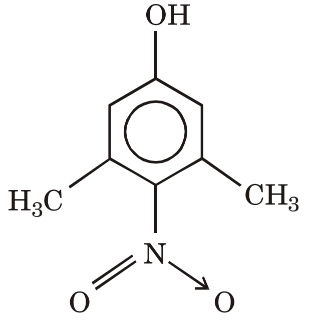


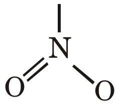


Which is more acidic ?

Solution :

(1) is more acidic than (2)

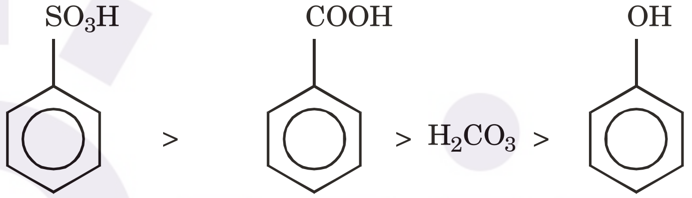




In (2) repulsion between CH_3 groups changes the plane of and it doesn't undergo resonance as porbitals are not in same plane.

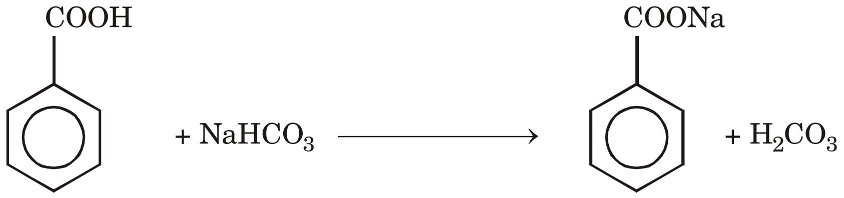
Therefore (1) is more acidic than (2)

Also remember



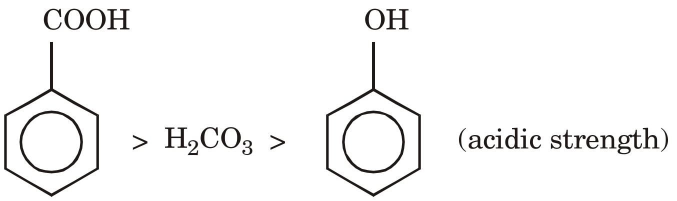
(acidity order)

Example 16



Which of the two reactions is feasible ?

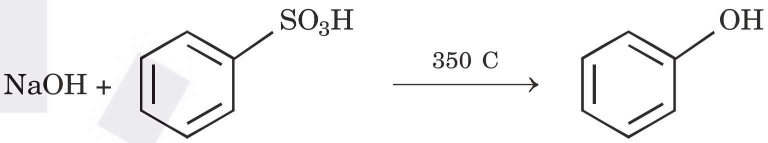
Solution :



Therefore only (2) is feasible.

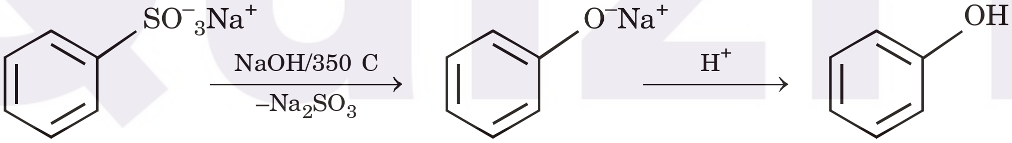
PREPARATION OF PHENOLS

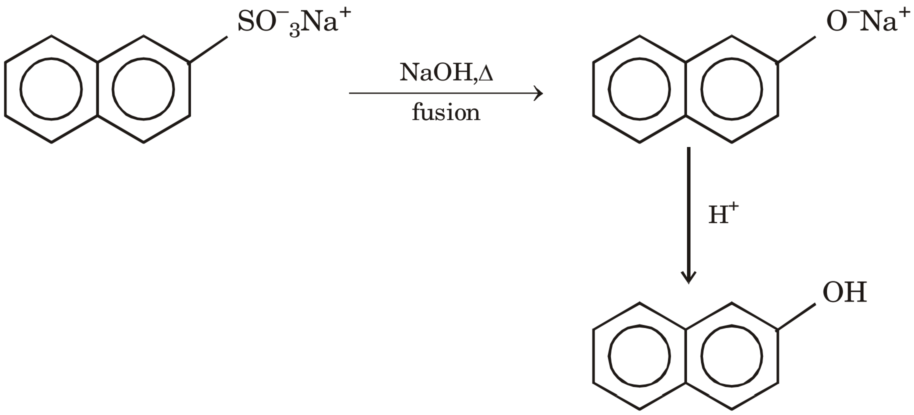
1. Reaction of Benzene Sulfonic Acid with Hydroxide



Reaction type : Nucleophilic Aromatic Substitution

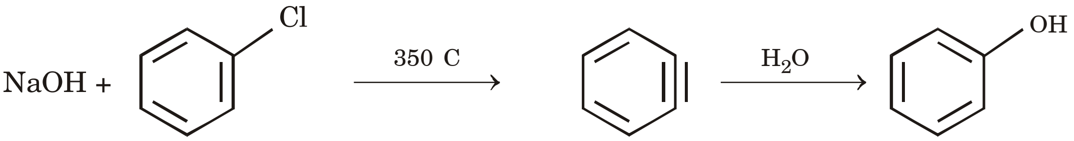
Mechanism :





Note : There an limitations to this method. Firstly, halophenols can not be prepared in this ways because at high temperature OH– displaces the halogens more readily than the replacement of SO_3^{2-} ion. Secondly, a substituent of – R type which is meta to the sulphonic acid group activates the ortho and para position for hydride displacement.

2. Base Hydrolysis of Chlorobenzene (Dow's Process)



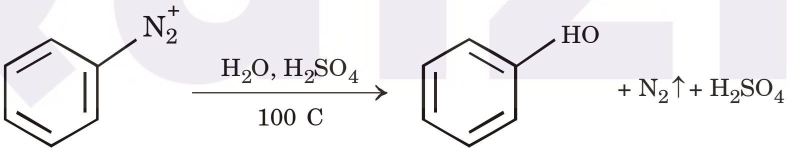
Reaction type : Nucleophilic Aromatic Substitution

Note :

- The reaction occurs via the elimination-addition mechanism via a benzyne intermediate.
- Elimination of HCl creates the benzyne that then undergoes addition of H_2O to produce the phenol.

3. Preparation of Phenols from Aryl Diazonium Salts

Benzene or arene diazonium salts on distillation with steam forms phenol or substituted phenols respectively, with liberation of nitrogen.

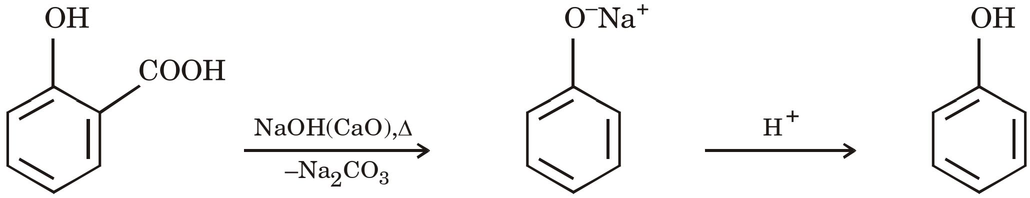


Note :

- Aryl diazonium salts can be converted into phenols using H_2O /H_2SO_4 / heat
- Aryl diazonium salts are prepared by reaction of aryl amines with nitrous acid HNO_2.

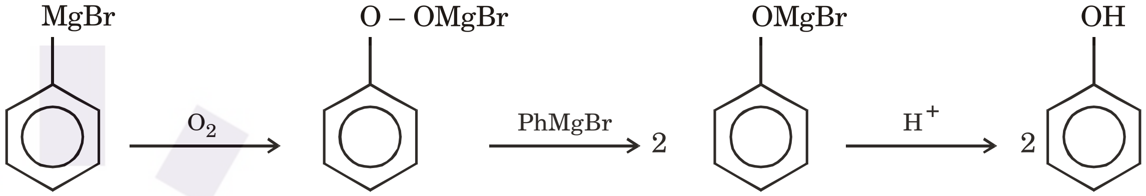
4. By Distillation of Phenolic Acids with Soda Lime

Phenolic carboxylic acids (ortho, meta or para) on heating with sodalime undergo carboxylation to give sodium phenoxide, which on acidification gives phenol.



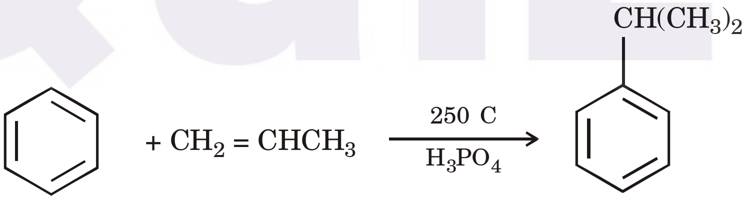
5. From Grignard Reagents

Phenyl magnesium halide or reaction with electrophilic O_2 gives a peroxide salt, which on reaction with another mole of phenyl magnesium halide gives 2 moles of magnesium salt of phenol. This on acidification gives 2 moles of phenol.

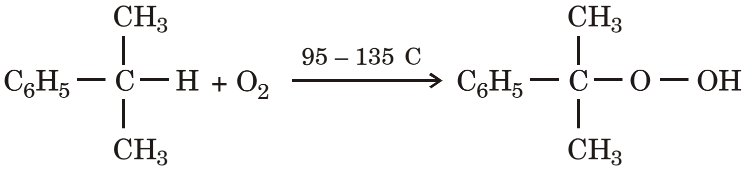


6. From Cumene Hydroperoxide

This is carried out by oxidising cumene to its hydroperoxide and subsequently decomposing it with acid into phenol and acetone. The mechanism involves 1, 2-shift of phenyl group.

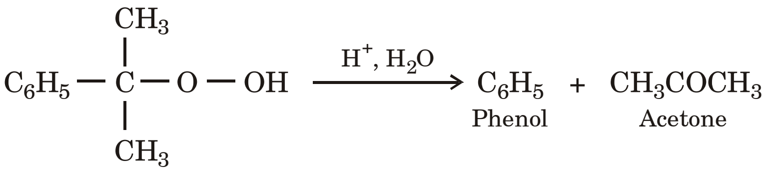


Isopropyl benzene
(Cumene)



$$C_6H_5-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-H + O_2 \xrightarrow{95-135\ C} C_6H_5-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-O-OH$$

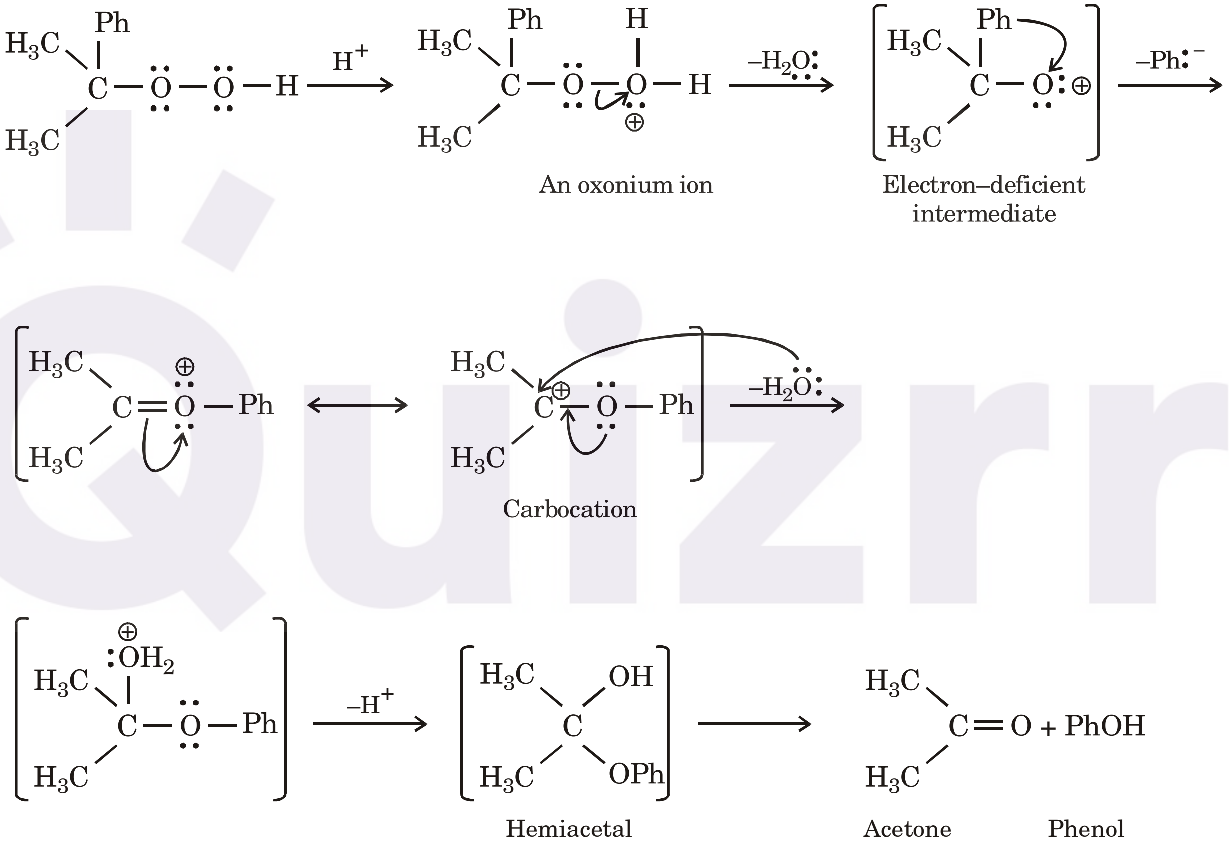
Cumene hydroperoxide



$$C_6H_5-C(CH_3)_2-O-OH \xrightarrow{H^+, H_2O} C_6H_5 + CH_3COCH_3$$

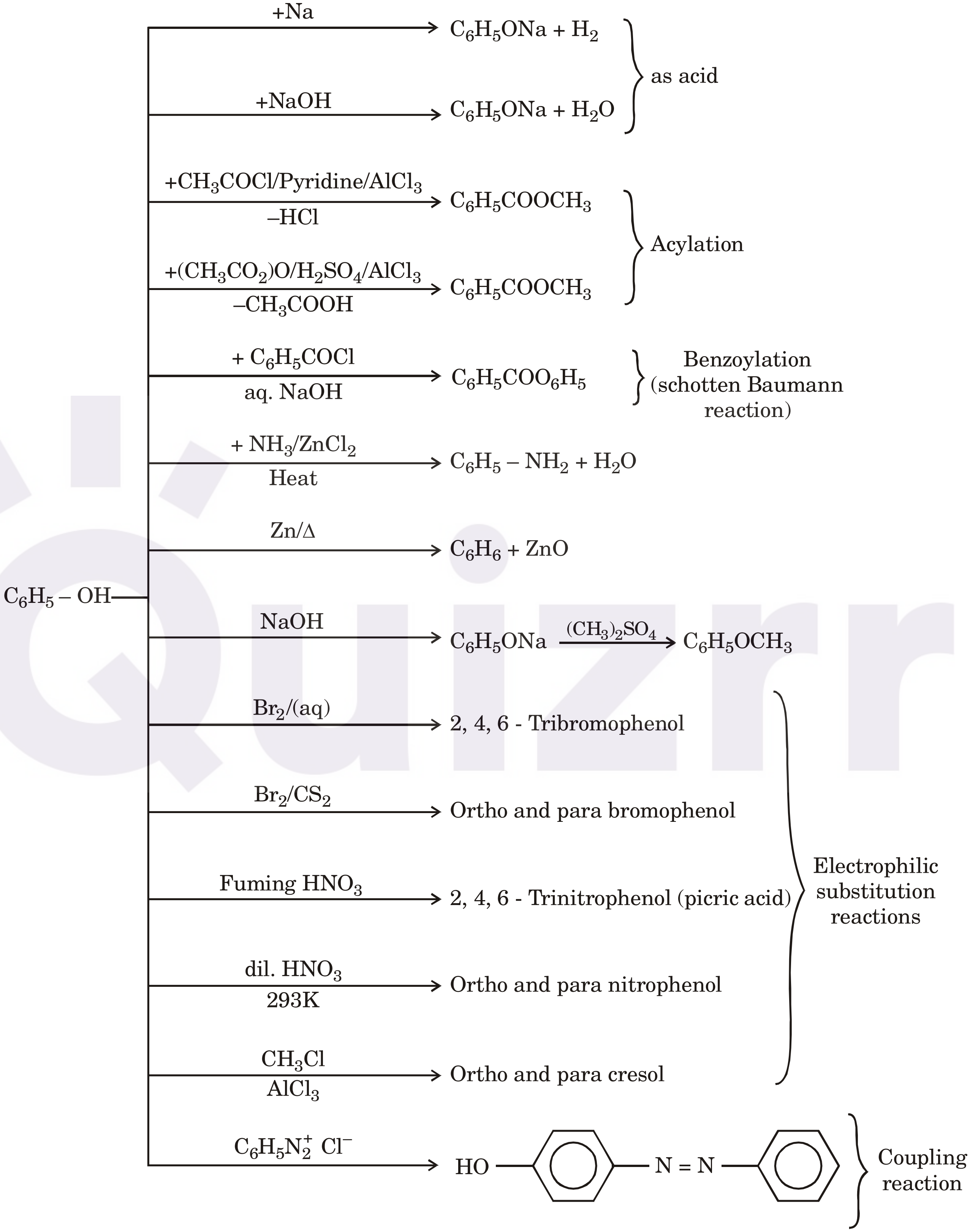
Cumene hydroperoxide

In the rearrangement, Ph migrates from carbon to oxygen. Most acid-catalyzed rearrangements require the intermediacy of a positively charged atom to which the group migrates, most of these positively charged sites were carbocations but in this case it is an O^+.



The rearrangement of Ph may be synchronous with the loss of H_2O.

REACTIONS OF PHENOL



$C_6H_5-OH \xrightarrow{+Na} C_6H_5ONa + H_2$

$C_6H_5-OH \xrightarrow{+NaOH} C_6H_5ONa + H_2O$

as acid

$C_6H_5-OH \xrightarrow[-HCl]{+CH_3COCl/Pyridine/AlCl_3} C_6H_5COOCH_3$

$C_6H_5-OH \xrightarrow[-CH_3COOH]{+(CH_3CO_2)O/H_2SO_4/AlCl_3} C_6H_5COOCH_3$

Acylation

$C_6H_5-OH \xrightarrow[aq.\ NaOH]{+\ C_6H_5COCl} C_6H_5COO_6H_5$

Benzoylation (schotten Baumann reaction)

$C_6H_5-OH \xrightarrow[Heat]{+\ NH_3/ZnCl_2} C_6H_5-NH_2 + H_2O$

$C_6H_5-OH \xrightarrow{Zn/\Delta} C_6H_6 + ZnO$

$C_6H_5-OH \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{(CH_3)_2SO_4} C_6H_5OCH_3$

$C_6H_5-OH \xrightarrow{Br_2/(aq)}$ 2, 4, 6 - Tribromophenol

$C_6H_5-OH \xrightarrow{Br_2/CS_2}$ Ortho and para bromophenol

$C_6H_5-OH \xrightarrow{Fuming\ HNO_3}$ 2, 4, 6 - Trinitrophenol (picric acid)

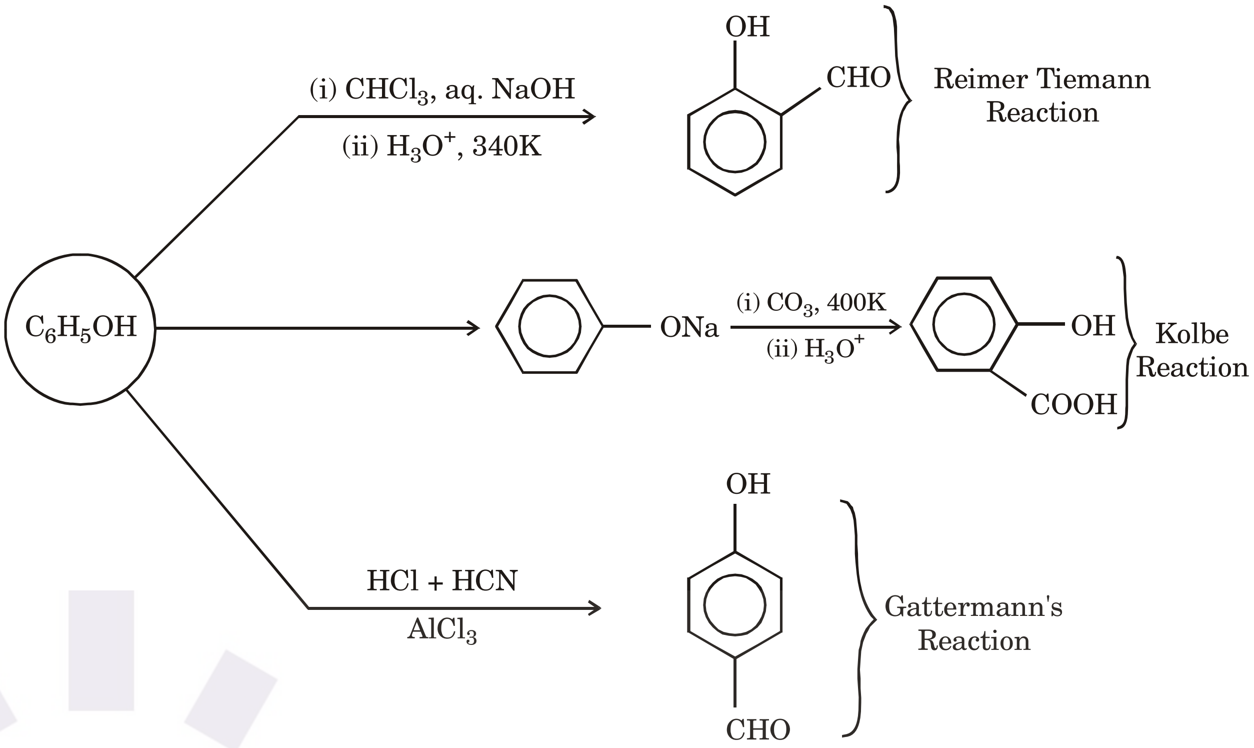
$C_6H_5-OH \xrightarrow[293K]{dil.\ HNO_3}$ Ortho and para nitrophenol

$C_6H_5-OH \xrightarrow[AlCl_3]{CH_3Cl}$ Ortho and para cresol

Electrophilic substitution reactions

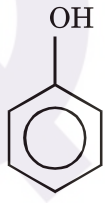
$C_6H_5-OH \xrightarrow{C_6H_5N_2^+\ Cl^-}$ HO–C₆H₄–N = N–C₆H₅

Coupling reaction



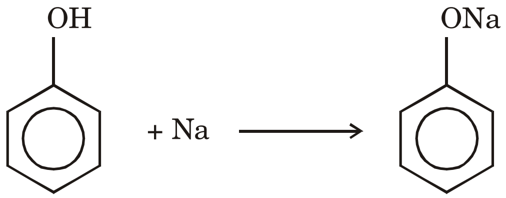
(i) Phenol as acid :

Order of acidity for following :

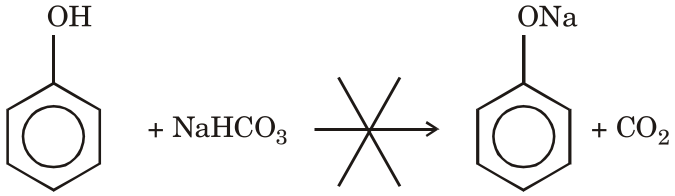
$H_2O <$


$< HCO_3^- < R\,COOH$

Hence,



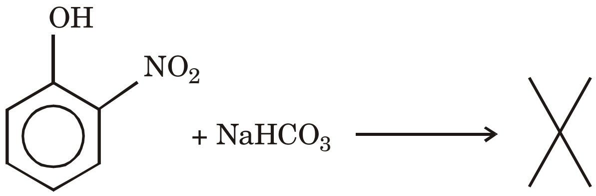
But



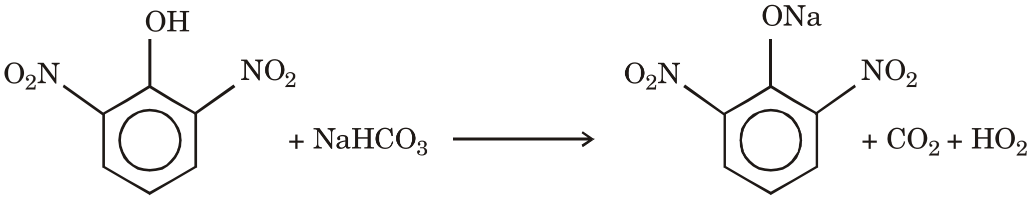
This reaction does not occur as HCO_3^- is a stronger acid than phenol.

Now, introducing electron– withdrawing groups increase the acidic strength of phenol in general.

(a)

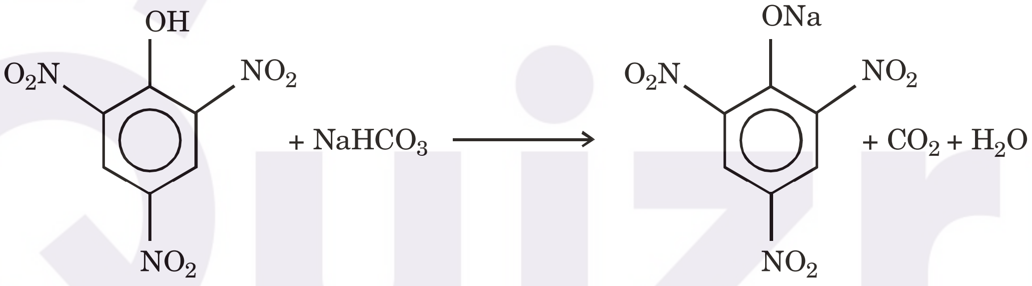


(b)

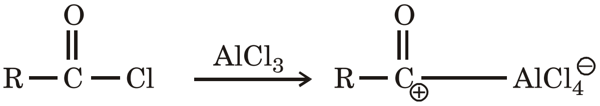


Now, 2 nitro groups make phenol more acidic than HCO_3^-.

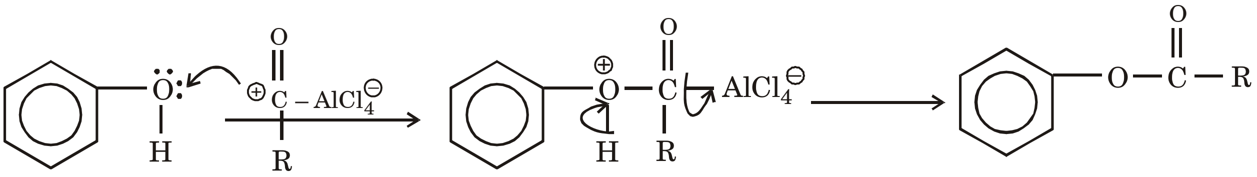
(c)



(ii) Acylation :

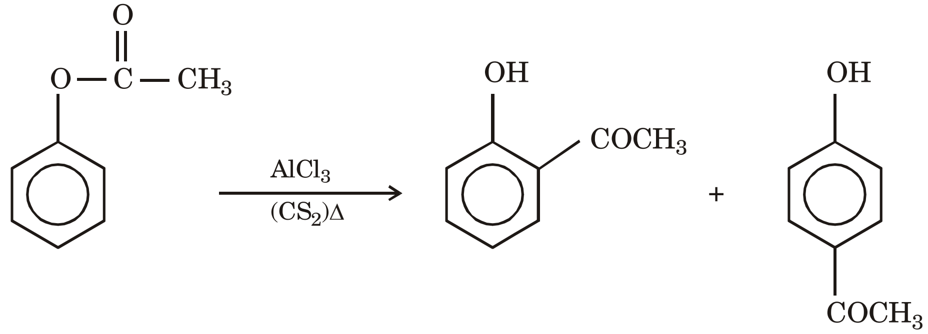


$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{AlCl_3} R-\overset{O}{\overset{\|}{C}}{}^{\oplus}\text{———}AlCl_4^{\ominus}$$



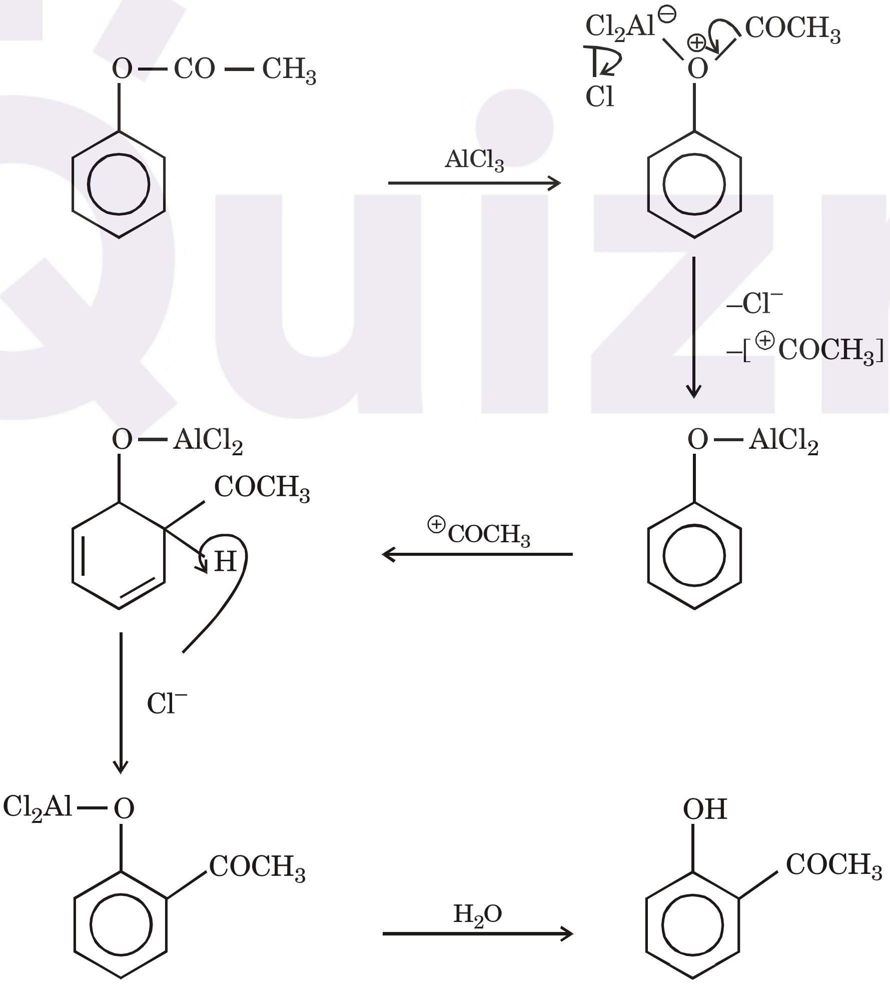
Important Point : It is also known the aryl esters in presence of $AlCl_3$ readily rearrange to form aryl ketones. This is known as the FRIES REARRANGEMENTS.

The reaction is :

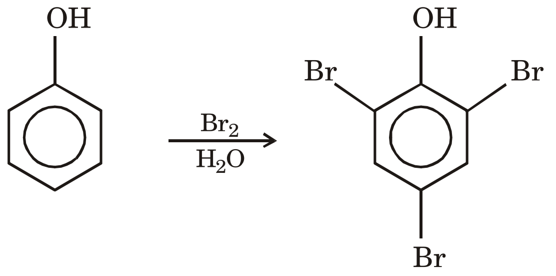


Generally low temperature (60 or less) favours the formation of the p-isomer whereas high temperature (above 160 C) favours the o-isomer.

Mechanism :



(iii) Bromination :

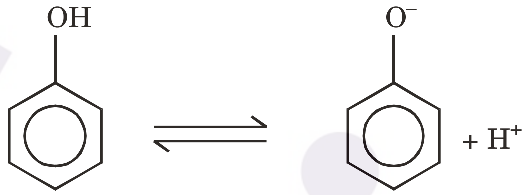


Mechanism :

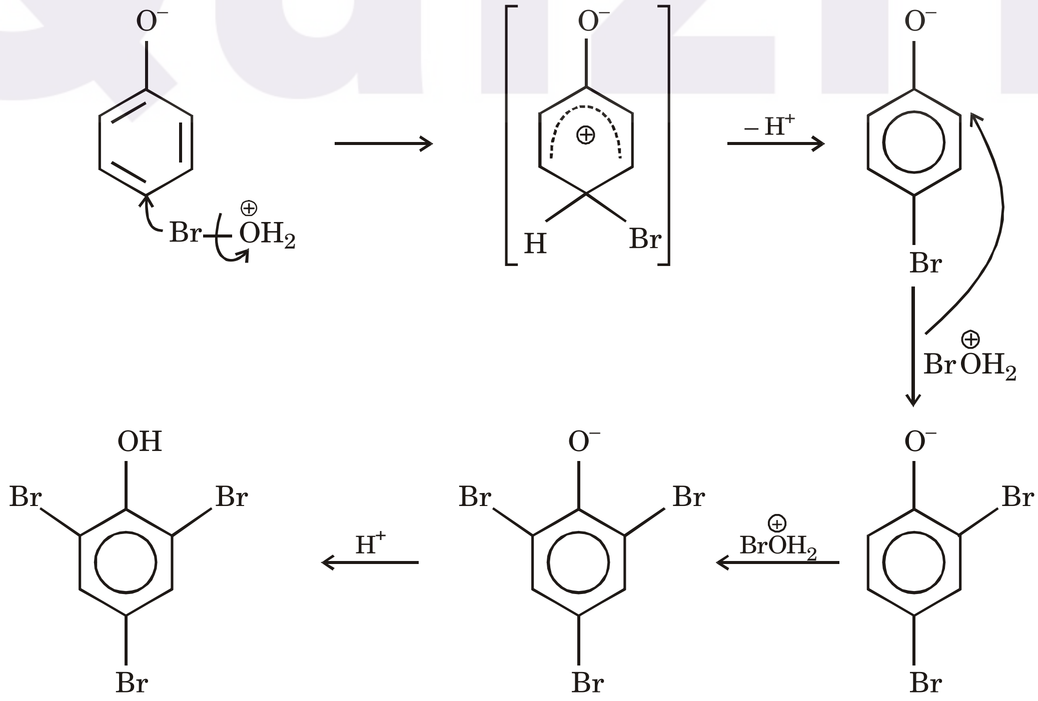
$$Br_2 + H_2O \rightleftharpoons HBr + HOBr$$

$$HOBr \xrightarrow{H^+ \text{ (from HBr)}} H_2\overset{\oplus}{O} — Br$$

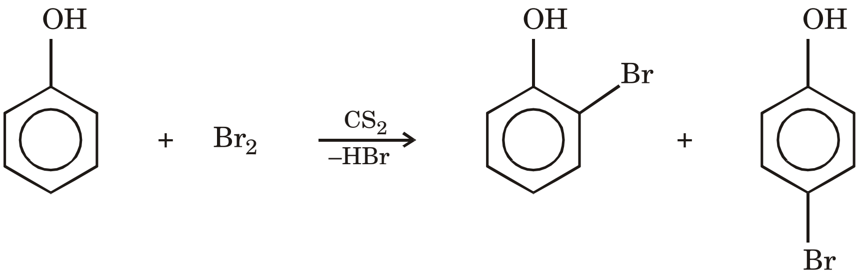
also,



{phenol in aqueous medium is partially ionized and phenoxide ion is more reactive than phenol itself towards electrophilic attack}.

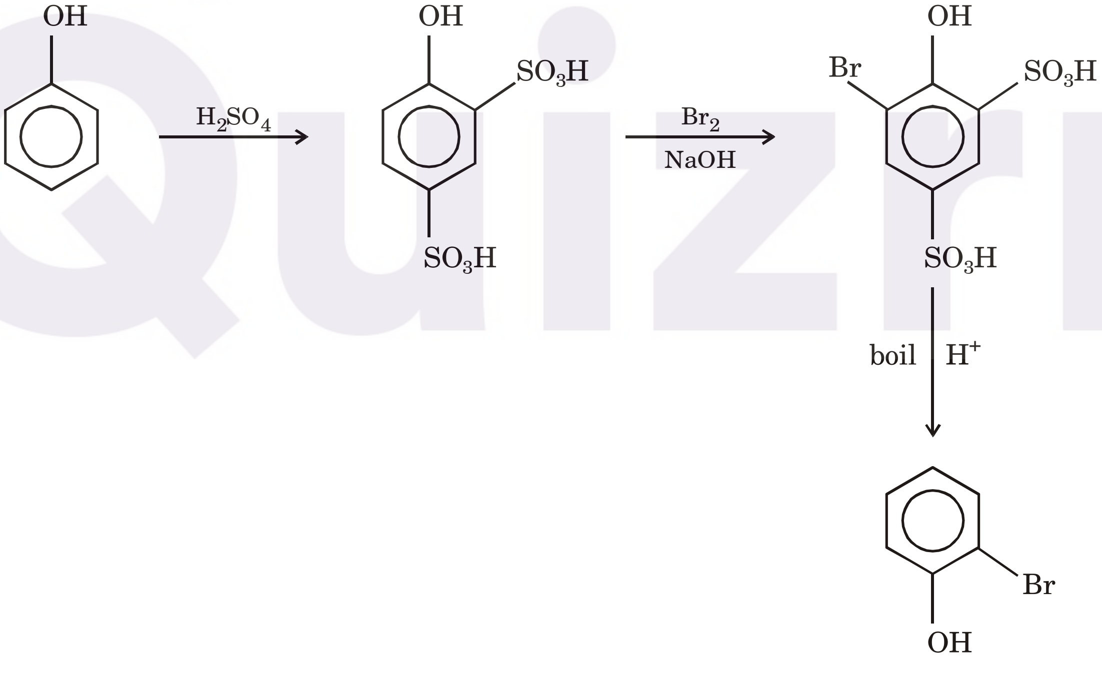


But in presence of non-aqueous medium like CS_2 or CCl_4, only mono-substitution takes place. This is because phenol is not ionized and hence benzene ring is less activated than that of phenoxide ion. Also, bromine in Br_2 is not as electrophiloic as in $Br — \overset{\oplus}{O}H_2$

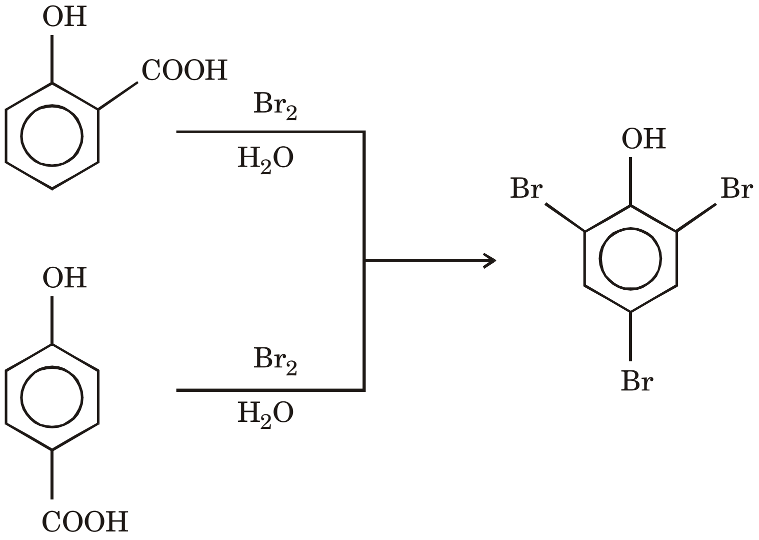


Now, if we have to prepare only the orthobromo phenol, then we wake use of protecting groups.

For example.



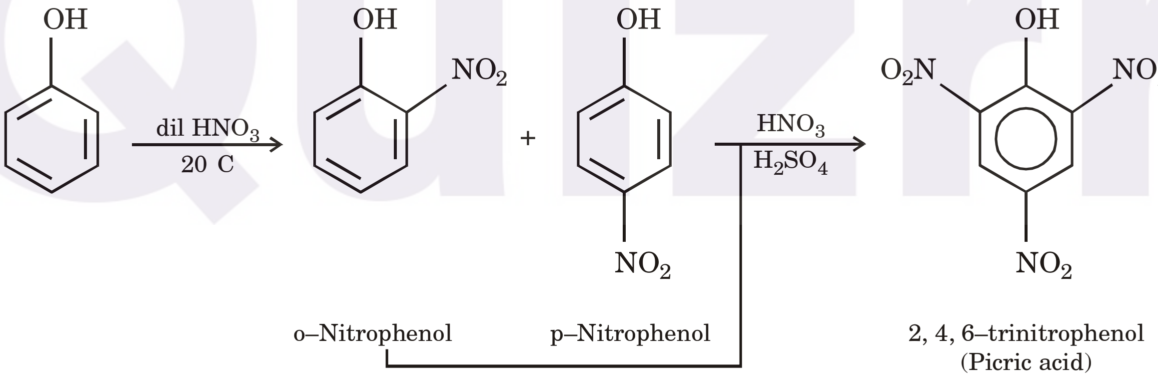
The activation of benzene ring in aqueous medium is so strong that derivatives of phenol containing — SO_3H group or — COOH group either at ortho or at para position are displaced by Br in bromination reaction.



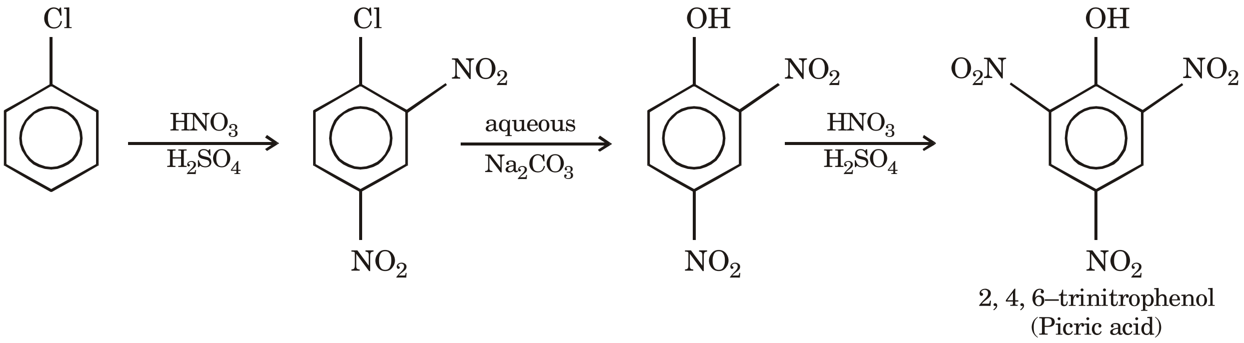
Trisubstitution of benzene is also observed in case of **aniline**, since aniline has same reactivity as that of phenoxide ion towards electrophilic attack.

(iv) Nitration

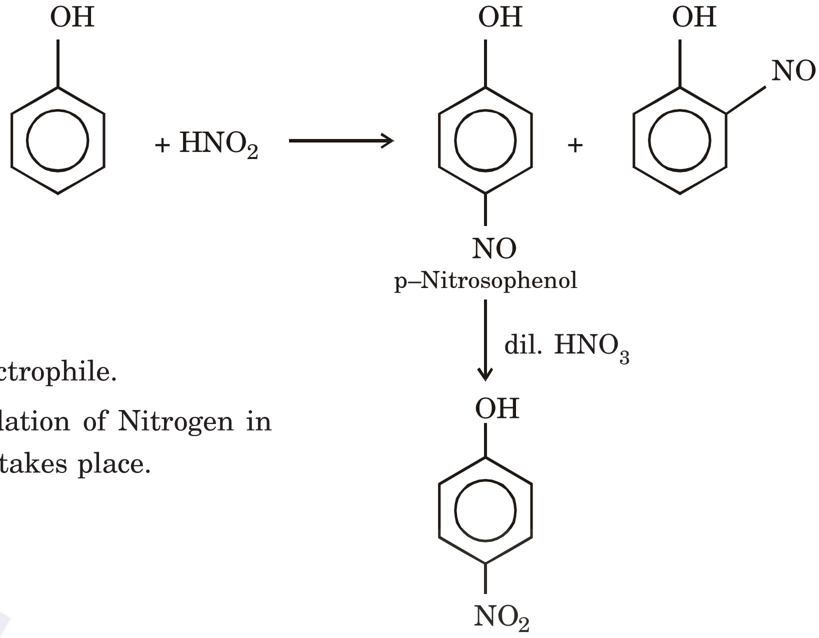
When treated with dilute HNO_3, phenol gives o and p-nitrophenol. When treated with nitrating mixture, phenol gives 2, 4, 6–trinitrophenol (picric acid) but the yield is poor.



Picric acid can be alternatively prepared as follows :

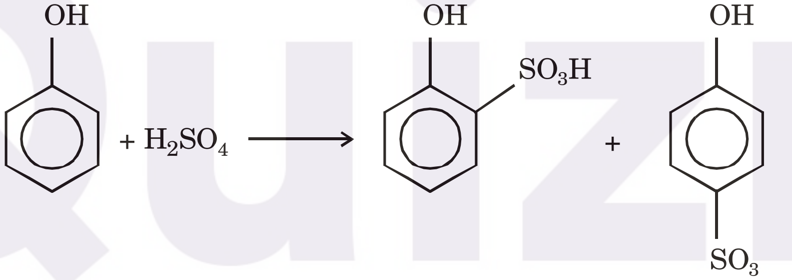


(v) Reaction with HNO_2 (Nitrosation)



- Here NO^+ is electrophile.
- In 2nd step oxidation of Nitrogen in p-nitrosophenol takes place.

(vi) Reaction with H_2SO_4 (SULPHONATION)



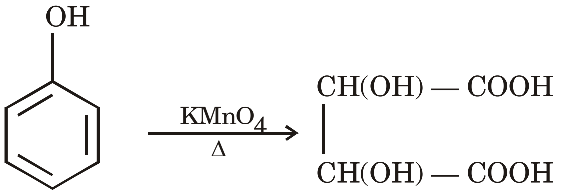
(ortho) (para)

At 25 C ortho will be major as it is kinetically controlled product.

At 100 C (high temperature) para will be major as it is thermodynamically controlled product.

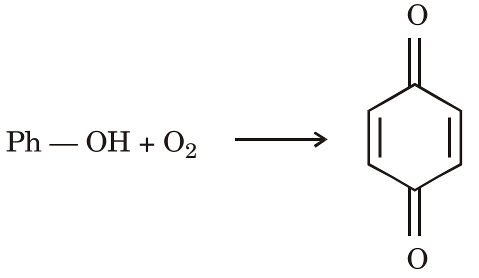
(vii) Oxidation by $KMnO_4$

Phenol can easily be oxidised by $KMnO_4$ and ring is broken



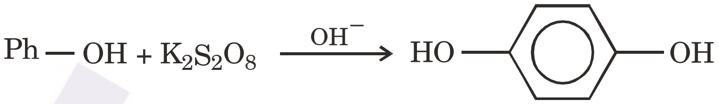
Meso tartaric acid

Oxidation with Air



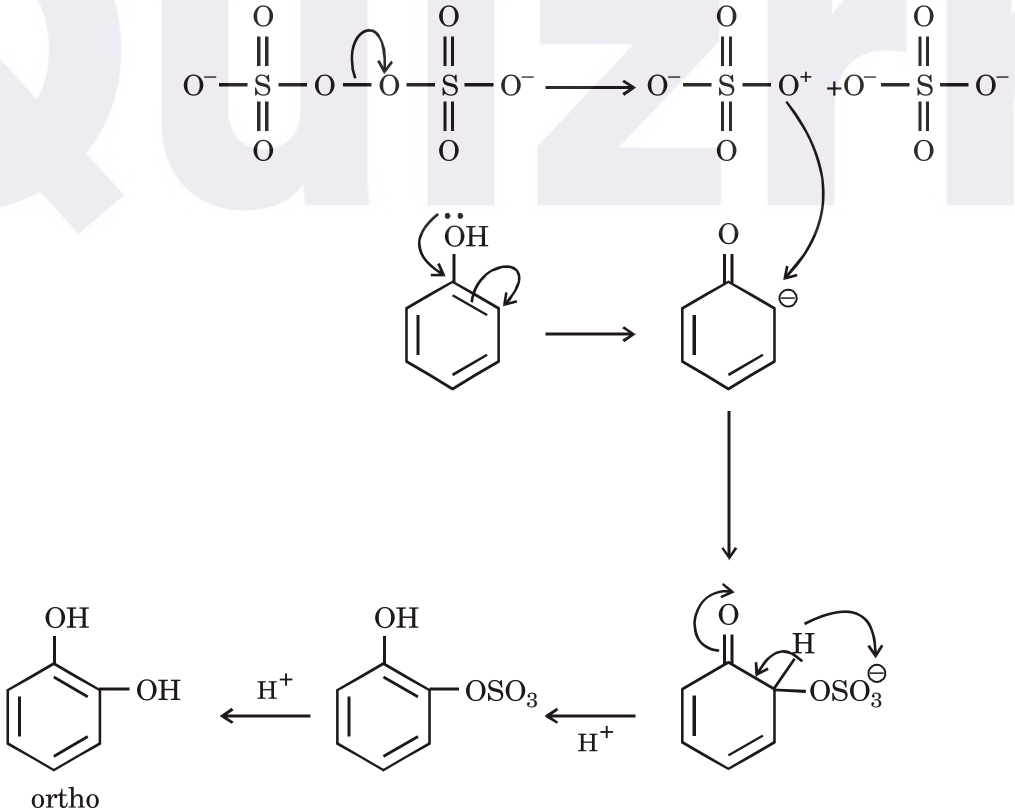
Benzoquinone

(viii) Action with bisulphate ion



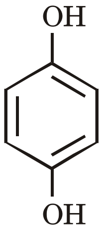
p–quinol

Mechanism :



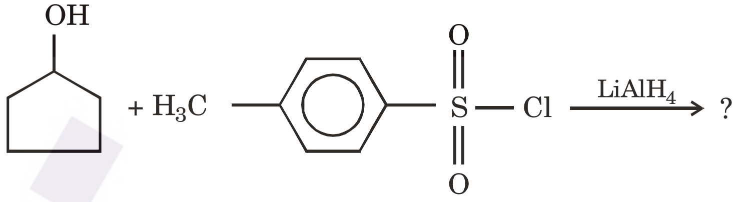
ortho

Similarly a para product can also be formed.

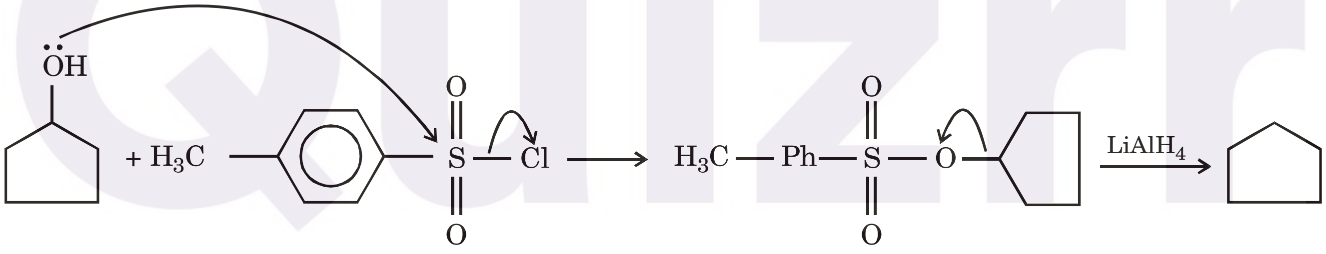


(major)

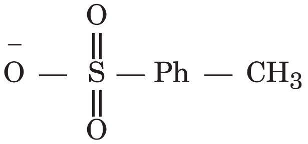
Example 17



Solution :



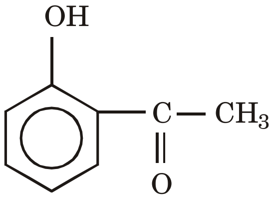
$LiAlH_4$ is source of hydride H^-.



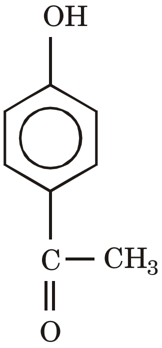
$\overset{-}{O} - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - Ph - CH_3$ is very good leaving group. Therefore it will leave very easily on attack of H^-.

Exmaple 18

Which has more B.P.



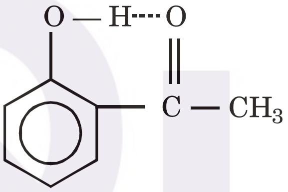
Or



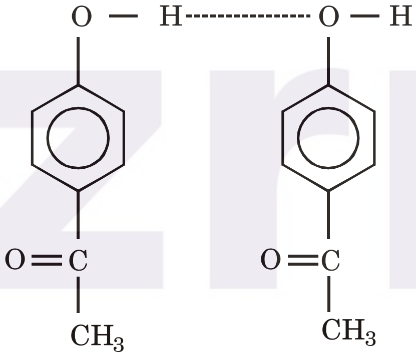
(a) (b)

Solution :

(a) has less b.p. than (b) due to intramolecular hydrogen bonding in (a) & intermolecular hydrogen bonding in (b)



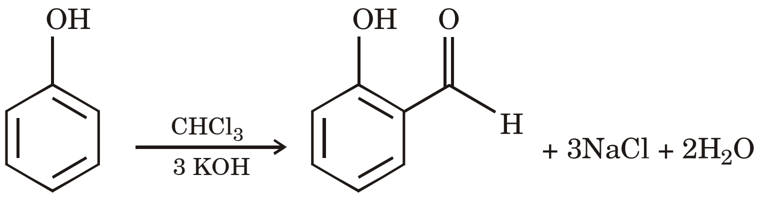
Intermolecular Hydrogen bonding



Intermolecular H bonding

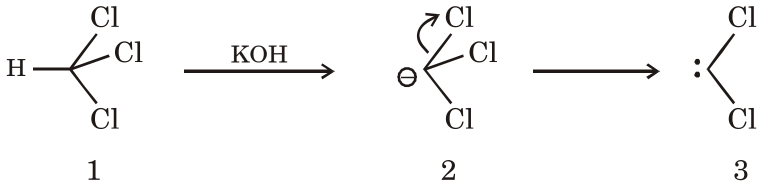
(ix) Reimer–Tiemann Reaction

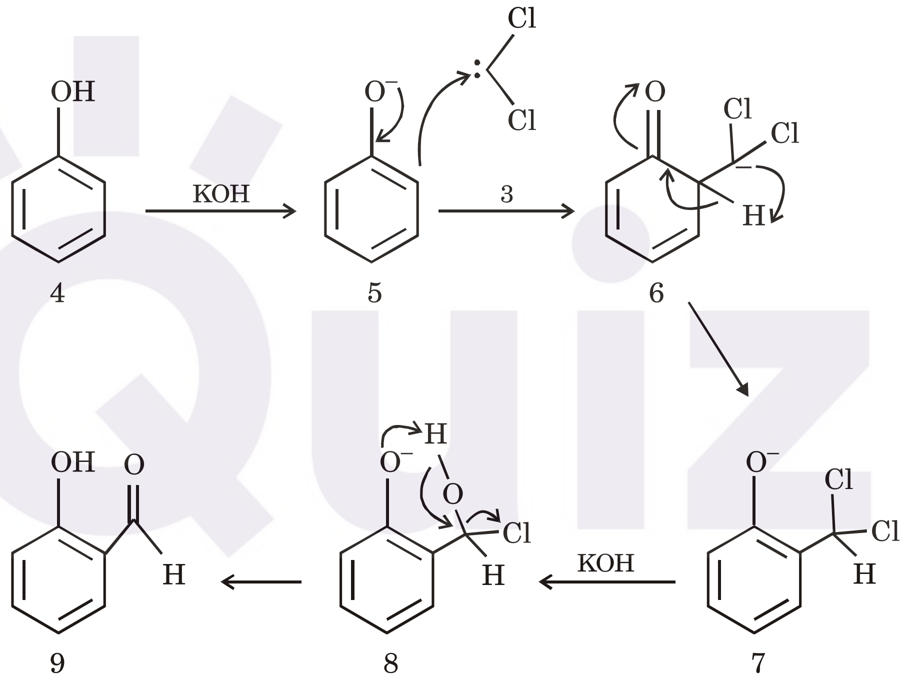
The Reimer–Tiemann reaction is a chemical reaction used for the ortho-formylation of phenols. In the simplest case, the product is salicylaldehyde :



Reaction mechanism

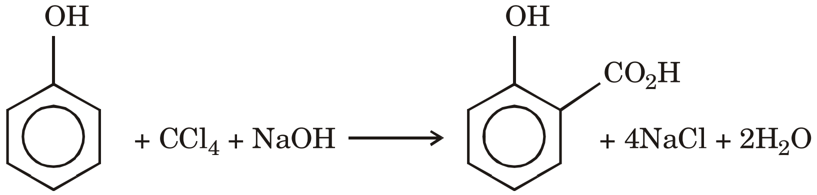
Chloroform (1) reacts with strong base to form the chloroform carbanion (2), which will quickly alpha-eliminate to give dichlorocarbene (3). Dichlorocarbene will react in the ortho-and para-position of the phenate (5) to give the dichloromethyl substituted phenol (7). After basic hydrolysis, the desired product (9) is formed.



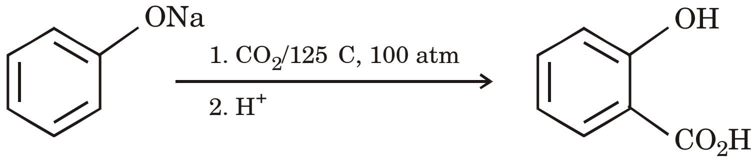


- o–hydroxy and p-hydroxy benzaldehyde are formed, which are separated by steam distillation.
- If o–positions are blocked, p-hydroxy benzaldehyde is the main product.

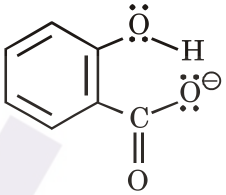
When phenol is refluxed with CCl_4 in alkaline medium, salicylic acid is formed.



(x) Carboxylation of Phenols (Kolbe-Schmitt reaction)

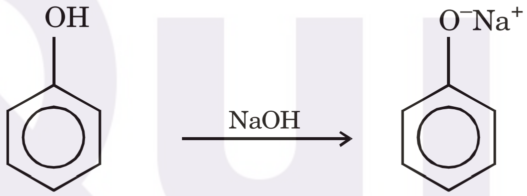


- Heating the nucleophilic phenolate salt with carbon dioxide under high pressure / temperature results in ortho-substitution.
- This process is also known as the Kolbe-Schmitt synthesis.
- o-hydroxybenzoic acid is more commonly known as salicyclic acid.

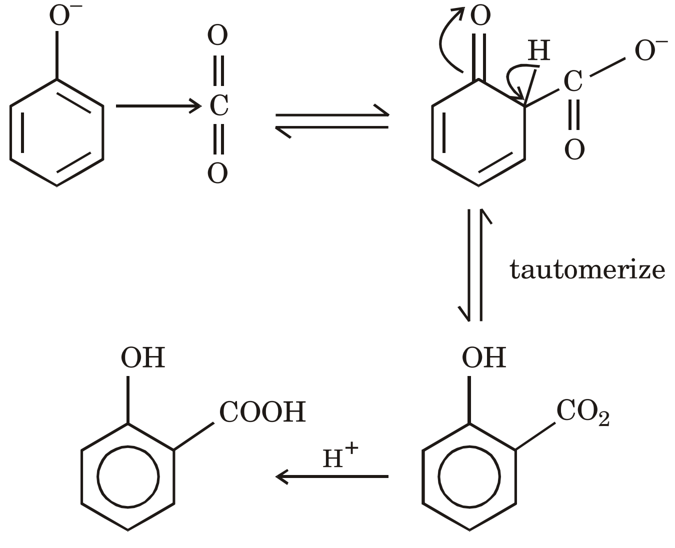


The geometry allows for an intramolecular hydrogen bond

Mechanism :

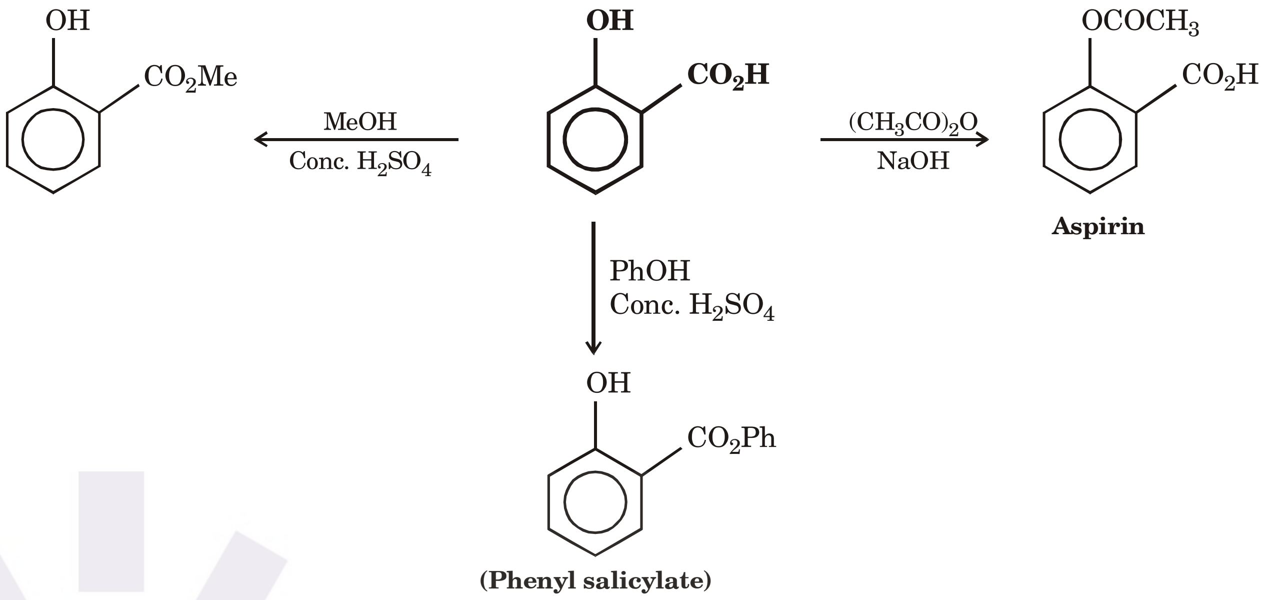


Now,



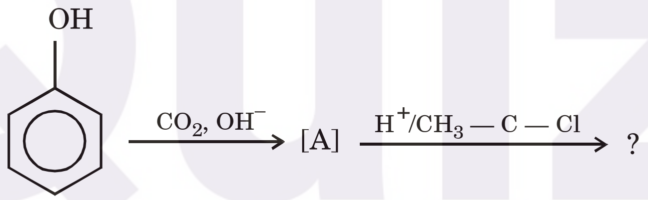
(salicylic acid)

Note : Salicylic acid is used for preparation of Asprin, oil of winter green (methyl salicylate) and Salol (phenyl salicylate)



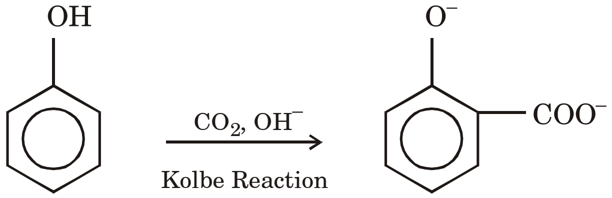
Example 19

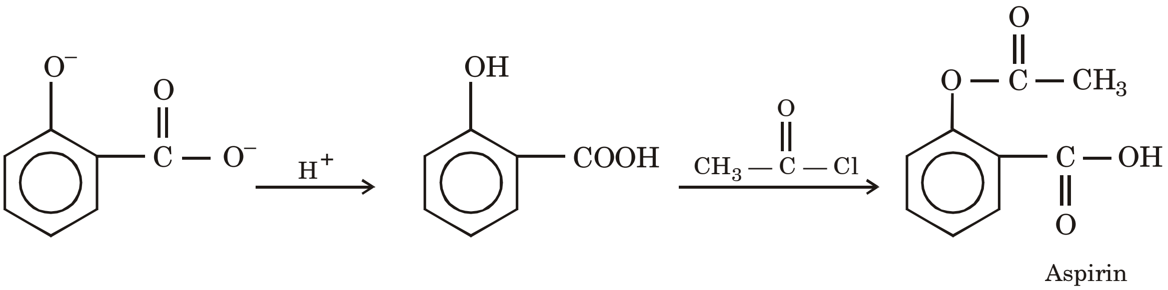
Find the final product



Solution :

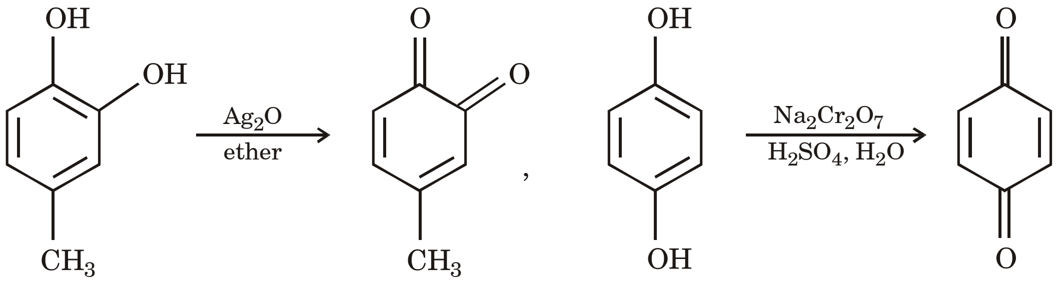
We know



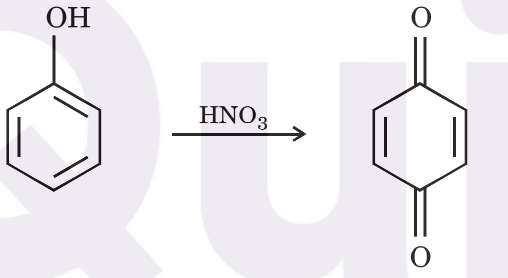


(xi) Oxidation of Phenols

- Oxidation can achieved by reaction with silver oxide (Ag_2O) or chromic acid ($Na_2Cr_2O_7$), or other oxidising agents.
- Particularly important are the oxidation of 1,2-and 1,4-benzenediol (pyrocatechol and hydroquinone, respectively) and their derivatives :

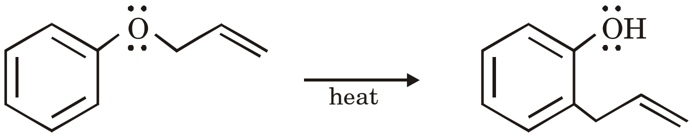


*** WITH HNO_3**



Benzoquinone

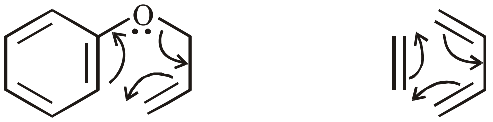
(xii) Claisen Rearrangment of Aryl Allyl Ethers :



Summary

- Aryl allyl ethers undergo a thermal rearrangement to give ortho-allylphenols.
- This reaction is an intramolecular process.

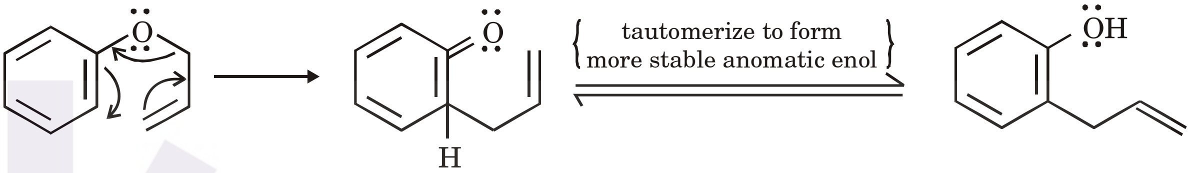
- Note how closely the mechanism of this reaction resembles that of the Diels-Alder reaction :



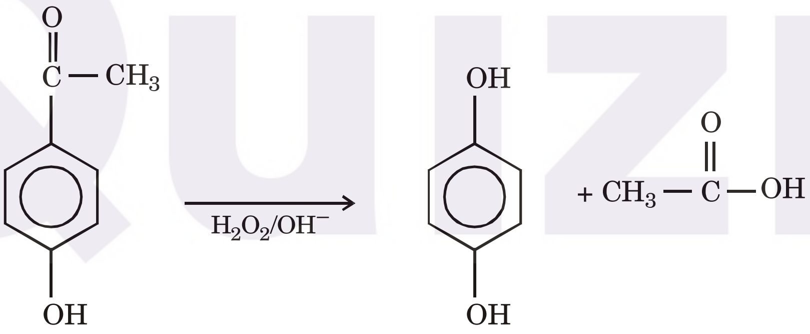
Claisen Diels-Alder

Caution : Do no confuse this reaction with the Claisen condensation of esters.

Mechanism :



(xiii) Dakin Reaction

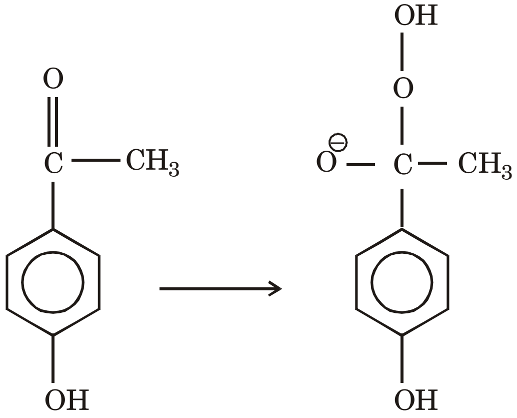


Mechanism :

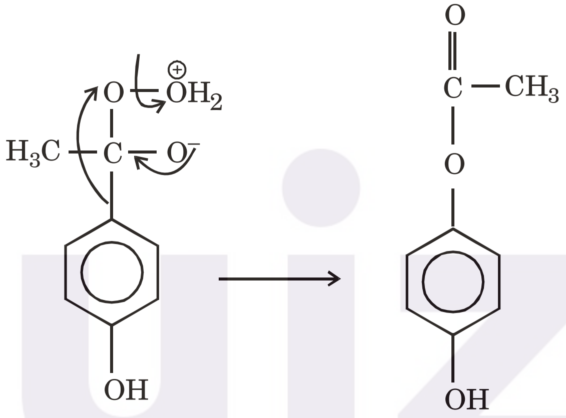
Step 1 : Formation of hypoperoxide ion

$$H_2O_2 + OH^- \longrightarrow {}^{-}O - O - H + H_2O$$

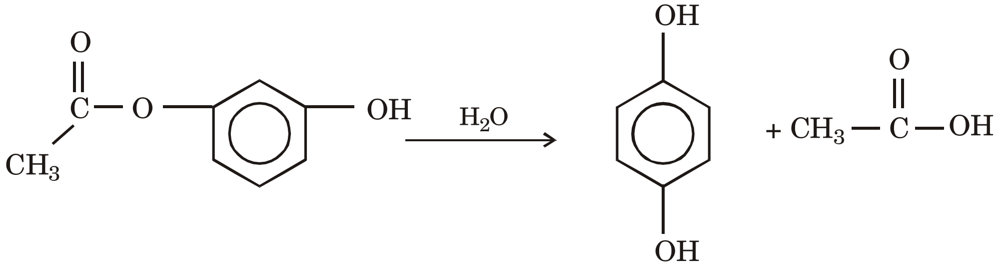
Step 2 : Attack on carbonyl group



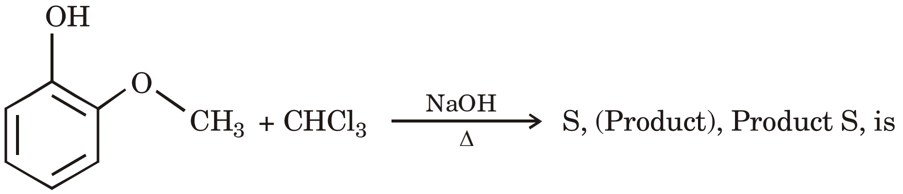
Step 3 : Shift of phenyl group.



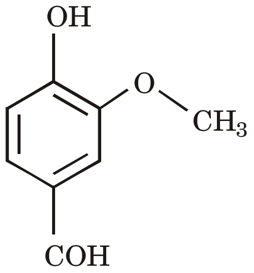
Setp 4 :



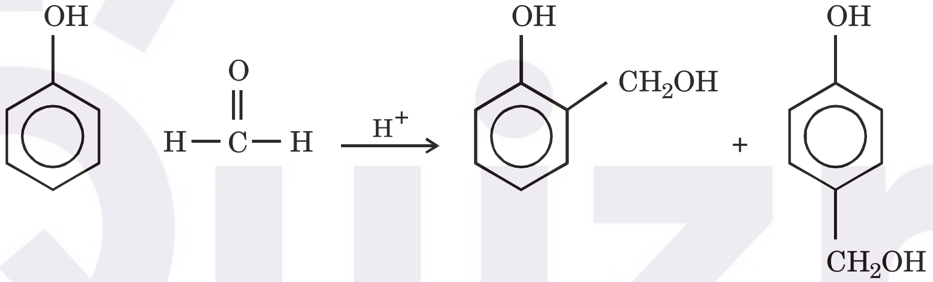
Example 20



Solution :

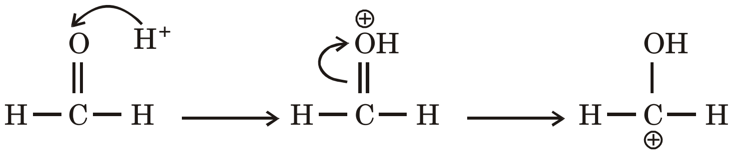


(xiv) Reaction with Formaldehyde

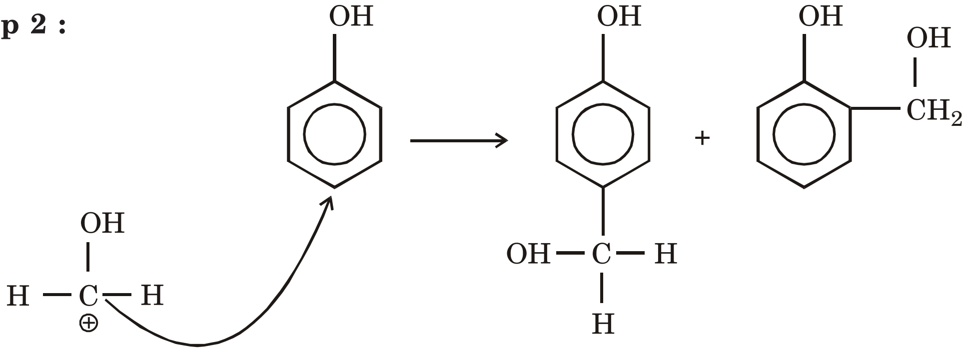


Mechanism :

Step 1 :

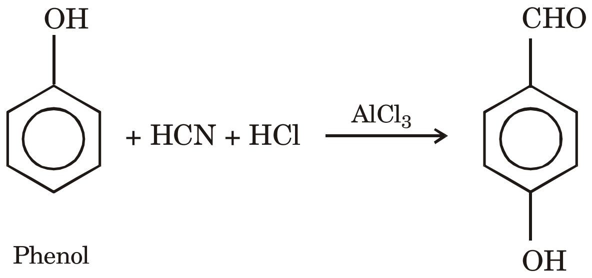


Step 2 :



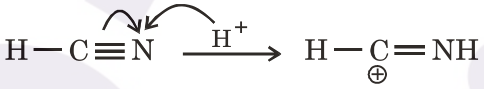
(xv) Gattermann Aldehyde Synthesis

When phenol is treated with liquid HCN and gaseous HCl in presence of anhydrous $AlCl_3$, product formed is hydrolysed Ph – hydroxy benzaldehyde

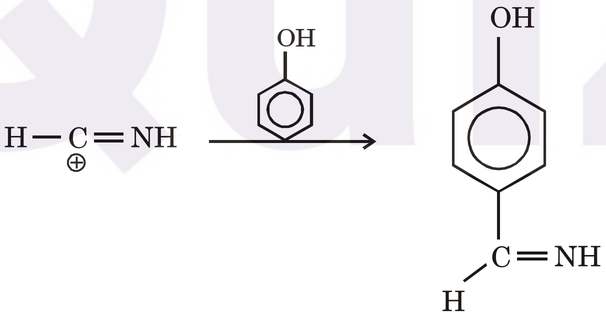


Mechanism :

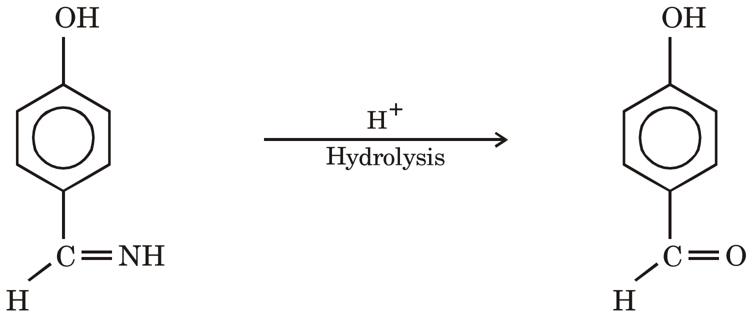
Step 1 : Formation of electrophile



Step 2 : Electrophulic substitution Reaction an Phenol

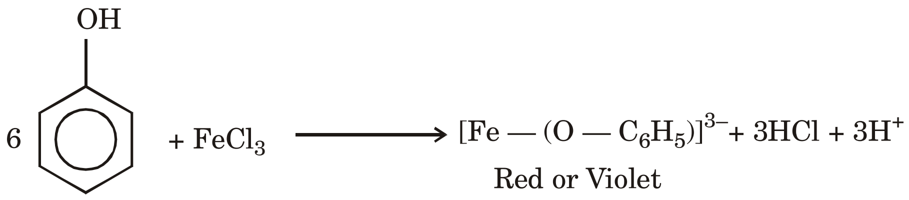


Step 3 :



Test of Phenol

1. Phenol reacts with $FeCl_3$ solution to form red and violet coloured solution.

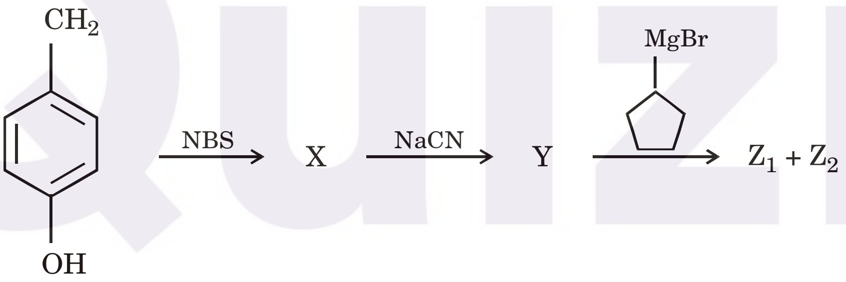


- This is also test for enol form.

2. **Liebermann Test :**

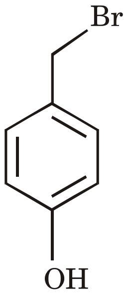
When phenol is dissolved in concentrated sulphuric acid and a few drops of aqueous sodium nitrite is added, a red colour is obtained on dilution and turns blue when aqueous sodium hydroxide is added.

Example 21

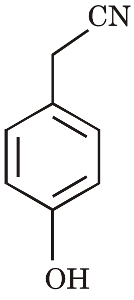


Solution :

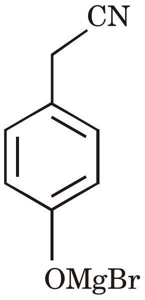
X =



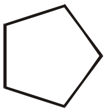
, Y =



, Z_1 =



, Z_1 =

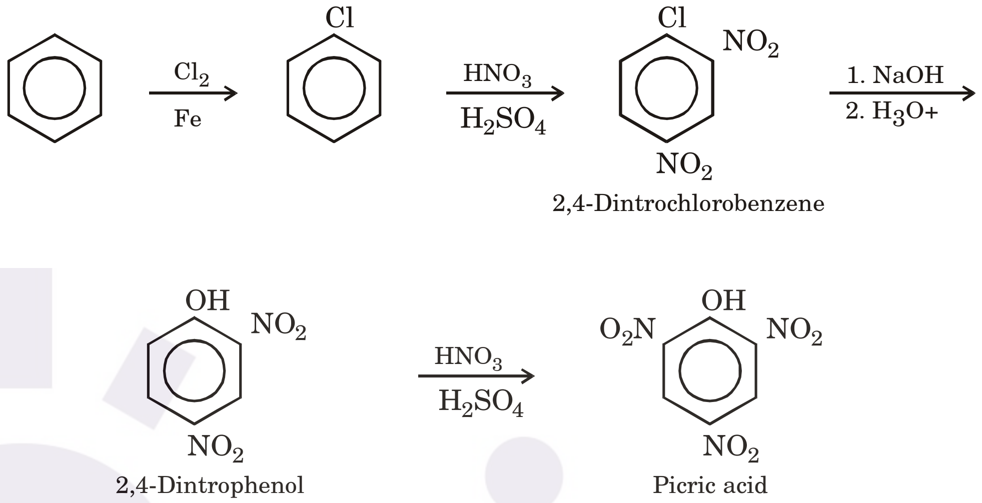


Example 22

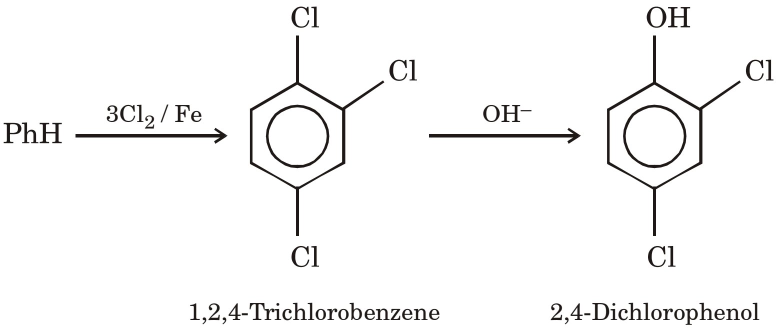
Prepare (a) Picric acid (2, 4, 6-trinitrophenol), and (b) 2, 4-dichlorophenol from benzene.

Solution :

Even through the NO_2's are in the o, o, p positions where OH directs electrophilic substitution, phenol cannot be nitrated because the **ring is susceptible to oxidative ring cleavage** by nitric acid. Instead, we take advantage of a nucleophilic addition – elimination.



PhCl cannot be trinitrated because the Cl and two NO_2's deactive the ring toward further electrophilic substitution. 2, 4-Dintrophenol can be nitrated because the two deactivating NO_2's prevent ring oxidation. (b) Phenol cannot be chlorinated because the ring is susceptible to oxidation by Cl_2. Again nucleophilic addition –elimination is used.

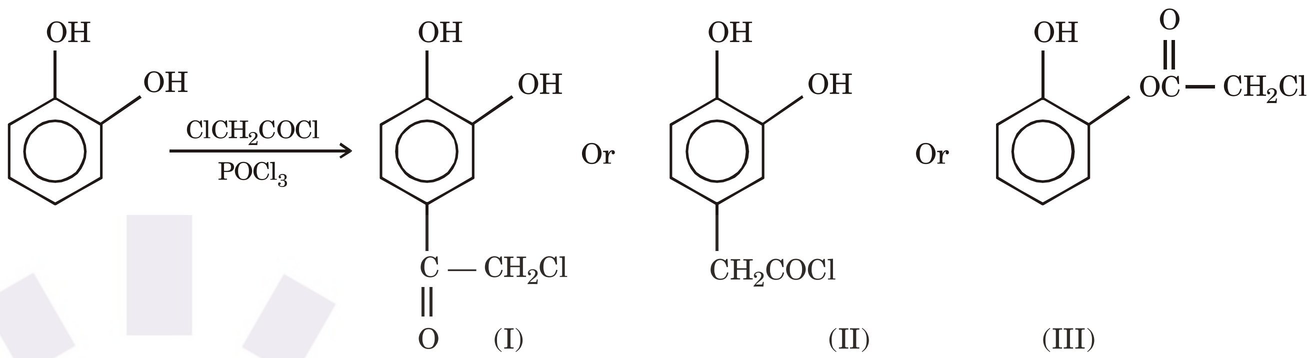


The displaced Cl is ortho to one other Cl and para to the other and is activated by both. Each of the other Cl's is meta to at least one deactivating Cl.

Example 23

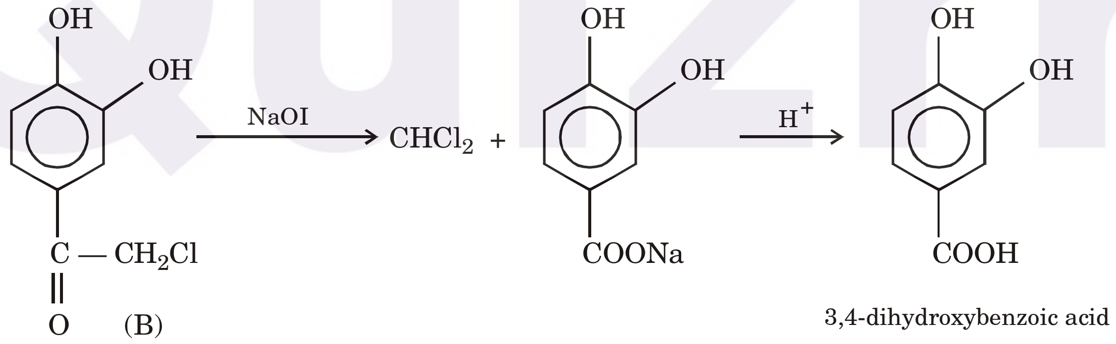
Compound (A), $C_9H_{13}O_3N$ shows optical isomerism when 1, 2-dihydroxybenzene is treated with chloroethanoyl chloride in the presence of $POCl_3$, compound (B), $C_8H_7O_3Cl$, is obtained which upon treatment with methyl amine gives compound (C), $C_9H_{11}O_3N$. Reduction of (C) with Pd/H_2 yields (A). Compound (B) when heated with NaOI and subsequent treatment of the product formed with dilute acid solution yields 3, 4-dihydroxybenzoic acid. Deduce the structure of (A).

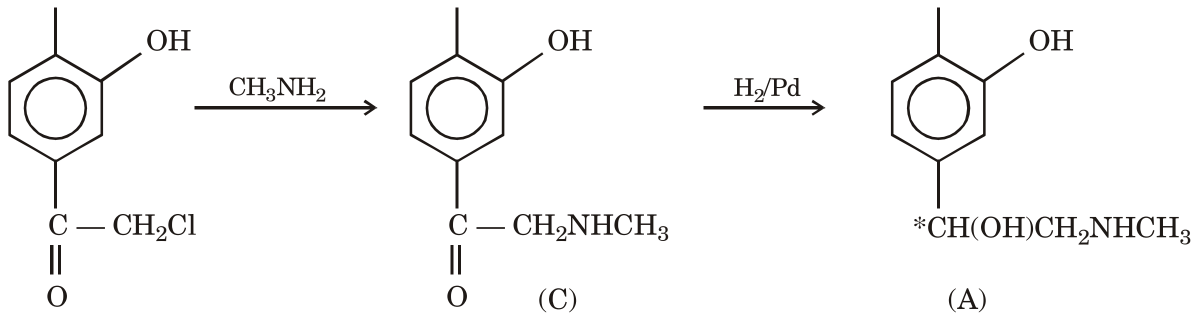
Solution :



1, 2–dihydroxybenzene may undergo ring acylation or ring alkylation or esterification to form compound (B).

Since (B) gives haloform test, the only possibility is (I).



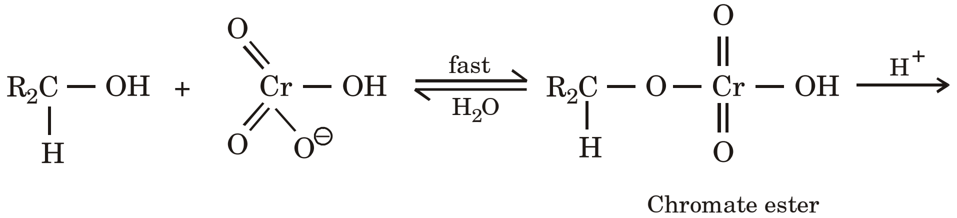


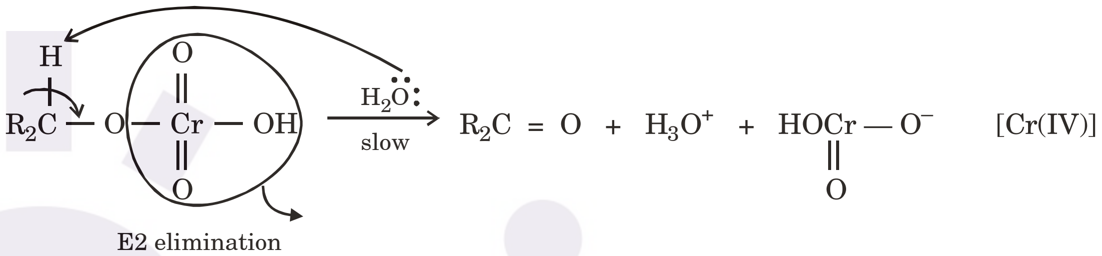
Example 24

Write mechanism for the oxidation of a 2 alcohol with Cr (VI) as $HCrO_4^-$.

Solution :

A chromate ester is formed in the first step :

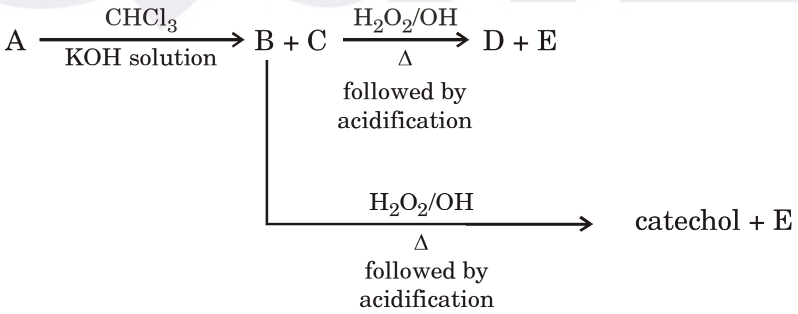




The Cr(IV) and Cr(VI) species react to form 2Cr(V), which in turn also oxidizes alcohols giving Cr(III) with its characteristics colour.

Example 25

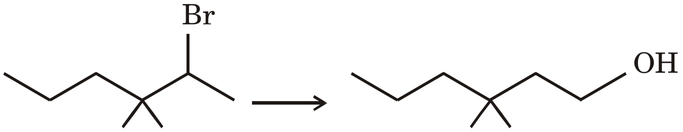
(a)



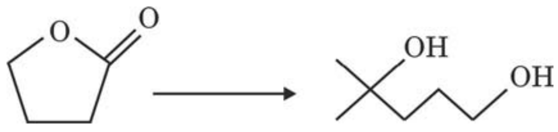
Identify A to E.

(b) Carryout the following transformations.

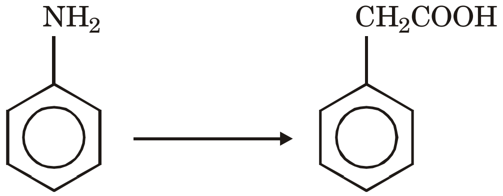
(i)



(ii)

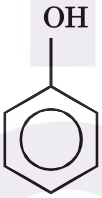


(iii)

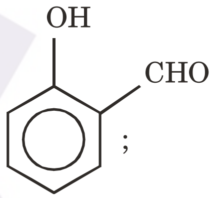


Solution :

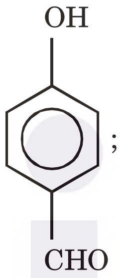
(a) A =



; B =



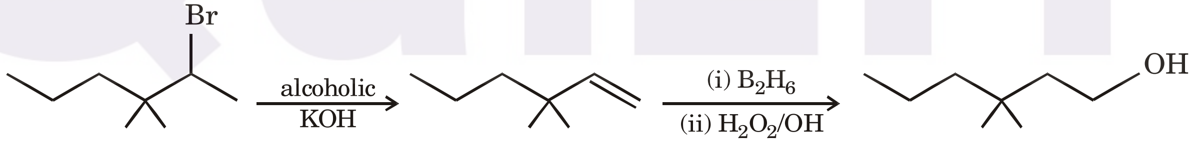
; C =



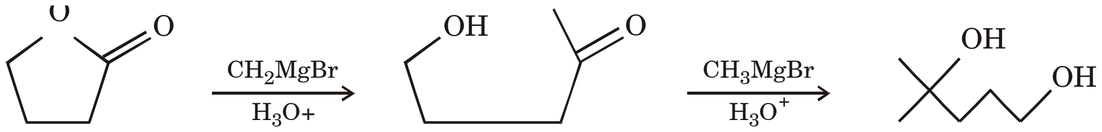
; D =

; E = HCO_2H

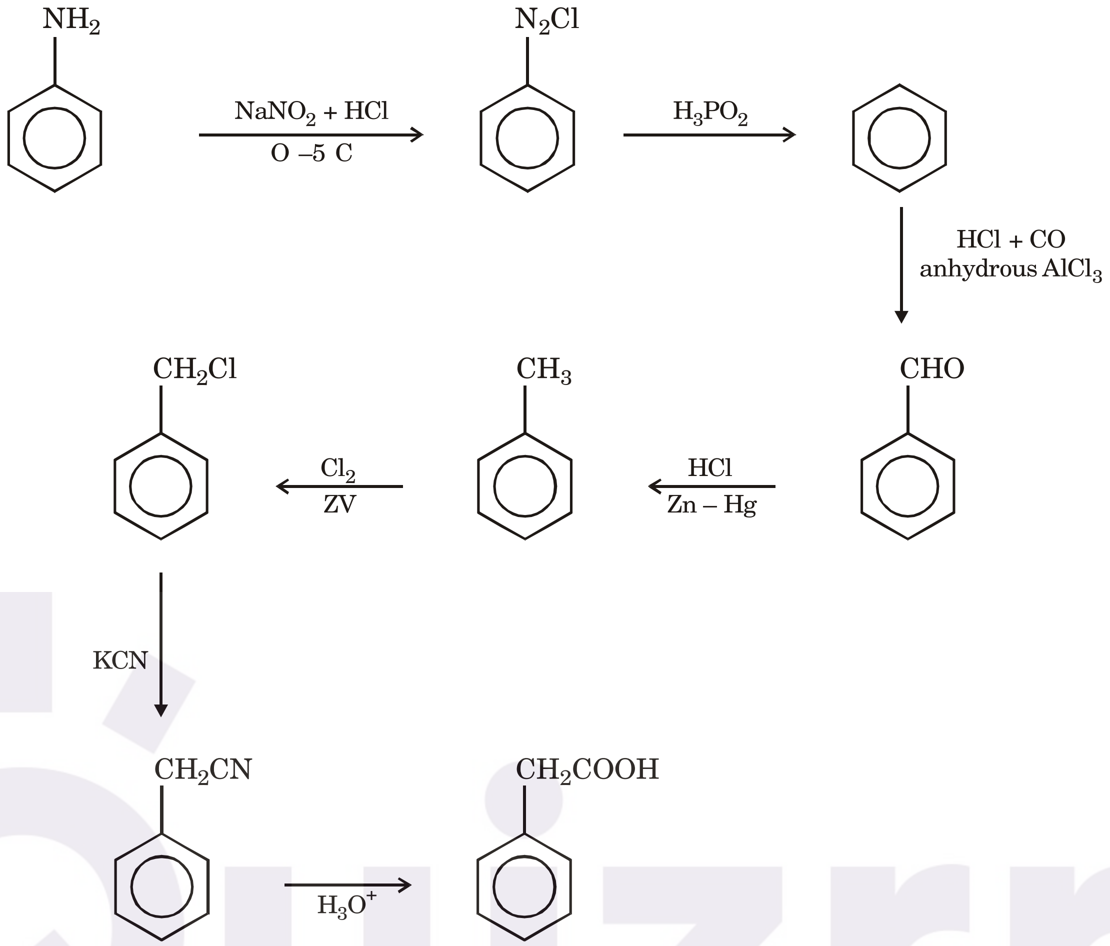
(b) (i)



(ii)



(iii)



Example 26

Give a simple test tube reaction that distinguishes between the compounds in each of the following pairs. What would you do, see and conclude ?

(a) t-butyl and n-butyl alcohol,

(b) ethyl and n-propyl alcohol,

(c) allyl and n-propyl alcohol,

(d) benzyl methyl ether and benzyl alcohol

(e) cyclopentanol and cyclopentyl chloride.

Solution :

(a) Add Acid $Cr_2O_7^{2-}$ (orange). The 1 n-butyl alcohol is oxidized; its solution changes colour to green Cr(III). The 3 t-butyl alcohol is unchanged. Alternatively, when Lucas reagent ($HCl + ZnCl_2$) is added, the 3 ROH quickly reacts to form the insoluble t-butyl chloride that appears as a second (lower) layer or a cloudiness. The 1 ROH does not react and remains dissolved in the reagent.

(b) Add I_2 in OH^- until the I_2 colour persists. A pale yellow precipitate of CHI_3 appears, indicating that ethyl alcohol is oxidized. n-Propyl alcohol does not have the — CH(OH) CH_3 group and is not oxidized.

(c) Add Br2 in CCl_4; as the Br_2 adds to the C = C of the colorless allyl alcohol, its orange colour disappears. The orange colour persists in the unreactive n-propyl alcohol.

(d) Add acid $Cr_2O_7^{2-}$. It oxidizes the alcohol, and the colour changes to green. The ther is unreactive. Alternately, if the two compounds are absolutely dry, add a small piece of Na to each. H_2 is released from the alcohol; the ether does not react.

(e) The simplest test is to add conc. H_2SO_4 to each dry compound. There will be only one layer as the alcohol dissolves, evolving some heat. The layers will be discernable for the chloride, which is not soluble in H_2SO_4.

Example 27

A compound (A), $C_{10}H_{12}O_2$, is soluble in aqueous NaOH, but does not dissolve in aqueous $NaHCO_3$. When (A) is treated with dimethyl sulphate and aqueous NaOH, compound (B), $C_{11}H_{14}O_2$, is formed with hot HI (A) gives methyl iodide and with hot and concentrated base, compound (C) $C_{10}H_{12}O_2$ is obtained. Compound (B) is insoluble in aqueous NaOH but readily decolourises $KMnO_4$ solution. When treated with hot and concentrated base, compound (B) produces (D), $C_{11}H_{14}O_2$. Ozonolysis of C produces a compound, which is isomeric with 4-hydroxy-3-methoxybenzaldehyde. Ozonolysis of (D) gives a compound, which is also obtained by treating 4-hydroxy-3-methoxybenzaldehyde with di-methyl sulphate. Deduce the structure of A with proper reasoning.

Solution :

Since (A) is soluble in aqueous NaOH, it is phenolic compound. Methylation with $(CH_3)_2SO_4$/ NaOH introduces – CH_3 group.

$\therefore$ (B) is $C_{11}H_{14}O_2$
(A) is $C_{10}H_{12}O_2$

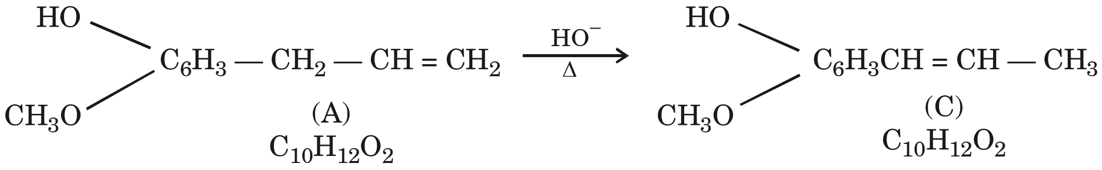
A difference of $-CH_2$ also indicates phenolic group in (A). (A) is cleaved with hot HI to produce CH_3I, indicating the presence of second oxygen.

That ozonolysis yields 4–hydroxy-3-methoxybenzaldehyde, indicates that (A) is trisubstituted benzene ring.

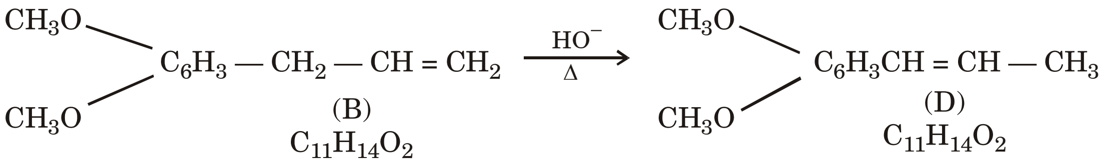
$$\begin{array}{c} C_{10}H_{12}O_2(A) \\ -OH \\ \hline C_{10}H_{11}O \end{array} \qquad \begin{array}{c} C_{10}H_{11}O \\ -OCH_3 \\ \hline C_9H_8 \end{array} \qquad \begin{array}{c} C_9H_8 \\ -C_6H_3 \\ \hline C_3H_5 \end{array} \qquad \text{(Trisubstituted aromatic ring)}$$

The residual group, C_3H_5 corresponds to an unsaturated side chain.

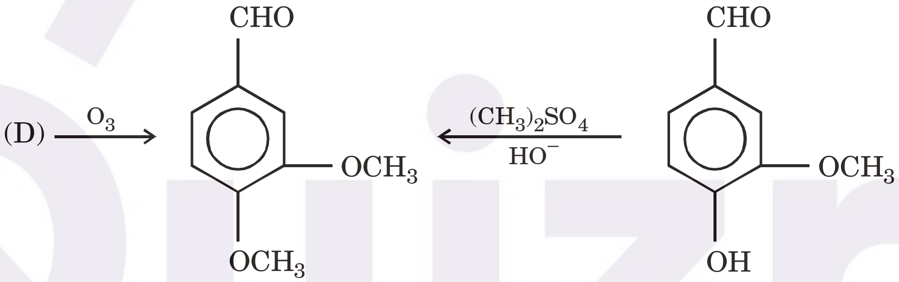
Treatment of (A) with strong and hot base results into isomerisation to C.

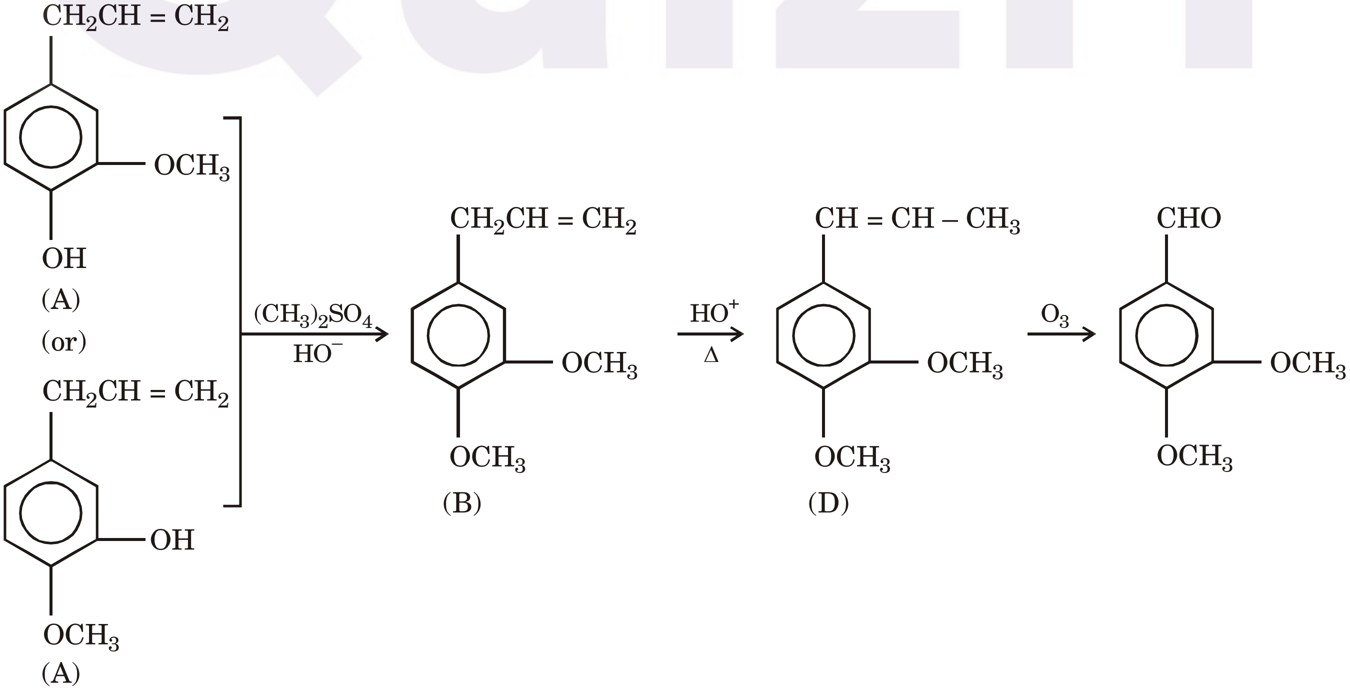


The same isomerisation occurs when (B) is treated with hot and concentrated base.

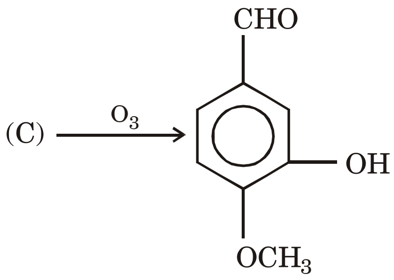


Orientation in the compounds can be worked out as follows :



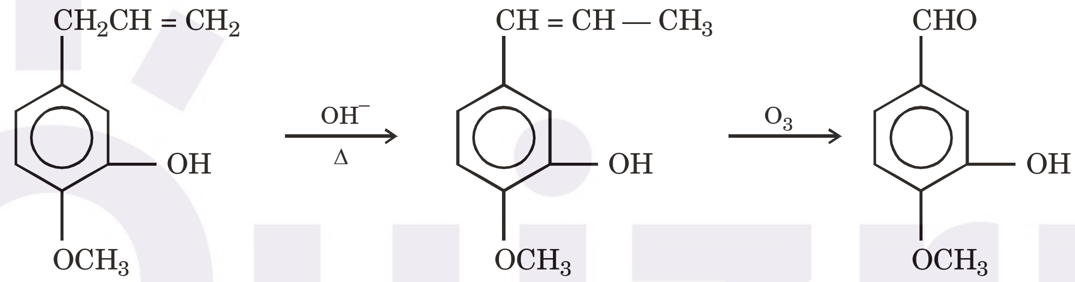


(C) has the same orientation of groups as (D). Hence the only possible isomer of 4-hydroxy–3–methoxybenzaldehyde that can be formed by cleavage of (C) is the one in which the –OH and $-OCH_3$ groups are reversed.



(isomer of 4–hydroxy–3–methoxybenzaldehyde)

Thus, A is



(A) (C) (D)

ETHERS

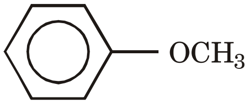
Ethers have a general formula R—O—R´. The groups R and R´ may be same or different and accordingly ethers are known as simple or mixed respectively. The general IUPAC name of ethers is alkoxy alkane

$CH_3 — O — CH_3$
Methoxy methane
(Dimethyl ether)

$CH_3 — O — C_2H_5$
Methoxy ethane

$CH_3CH_2CH_2 — OC_2H_5$
Ethoxy propane

$CH_2 = CH — OC_2H_5$
ethoxyethene



Methoxy benzene
(anisole)

Physical Properties

- The polar nature of the C–O bond (due to the electronegativity difference of the atoms) results in intermolecular dipole-dipole interactions.
- An ether cannot form hydrogen bonds with other ether molecules since there is no H to be donated (no – OH group)
- Ethers can be involved in H-bonding with systems able to donate H (e.g. water).
- The implications of these effects are :
  - lower melting and boiling points compared to analogous alcohols.
  - solubility in aqueous media similar to analogous alcohols.
- Ethers have a definite dipole moment. This is due to the bent structure of their molecule.
- They are lighter than water. Their density incolases with increase in molecular mass.

Reactivity :

- The ethereal O atom is a region of high electron density due to the lone pairs.
- Ether oxygen atoms are Lewis bases.
- Like an alcohol – OH group, the – OR group is a poor leaving group and needs to be converted to a better leaving group before substitution can occur.
- The most important reaction of ethers is their cleavage by strong acids such as HI or HBr.

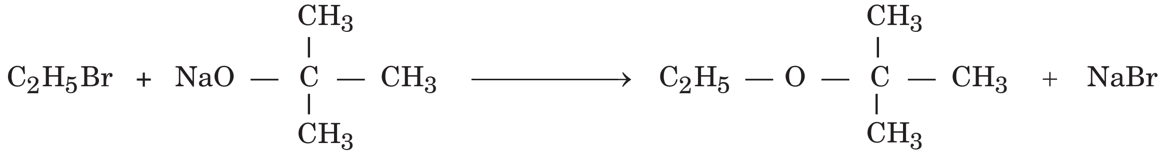
Methods of Preparation :

1. By Williamson Synthesis :

$$R — X + R'ONa \longrightarrow R — O — R' + NaX$$

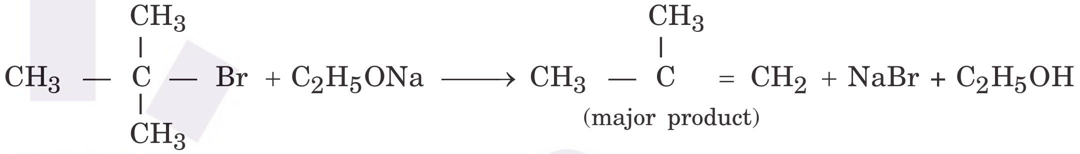
Here –X can be halides, sulphates ($-OSO_2OR$) or sulphonates ($-OSO_2R$). Also, the temperature should be low for this reaction.

The alkyl halide used in this reaction should preferably be primary because in case of secondary and tertiary alkyl halides, the elimination reaction predominates resulting in the formation of alkene as the major product.



$$C_2H_5Br + NaO - \overset{CH_3}{\underset{CH_3}{C}} - CH_3 \longrightarrow C_2H_5 - O - \overset{CH_3}{\underset{CH_3}{C}} - CH_3 + NaBr$$

Whereas,



$$CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - Br + C_2H_5ONa \longrightarrow \underset{\text{(major product)}}{CH_3 - \overset{CH_3}{C} = CH_2} + NaBr + C_2H_5OH$$

Note : (1) For aromatic ethers generally alkyl sulphates are used.

(2) The reaction is S_N2.

2. Dehydration of alcohols

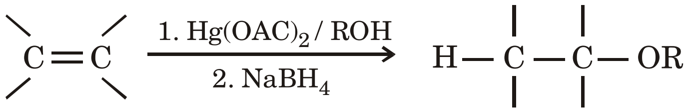
$$\underset{\text{(excess)}}{2C_2H_5OH} \xrightarrow[413\,K]{\text{conc. } H_2SO_4} C_2H_5 - O - C_2H_5 + H_2O$$

$$2C_2H_5OH \xrightarrow{Al_2O_3} C_2H_5 - O - C_2H_5 + H_2O$$

Dehydration of alcohols to ether is an example of nucleophillic substitution. However, it can be used only to prepare symmetrical ethers only, otherwise we get a mixture of ethers. For example,

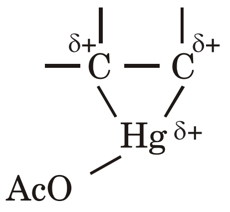
$$R - OH + HOR' \xrightarrow[140\ C,\ \Delta]{\text{conc. } H_2SO_4} R - OR + R'OR + R'OR'$$

3. Alkoxy Mercuration - Demercuration of Alkenes



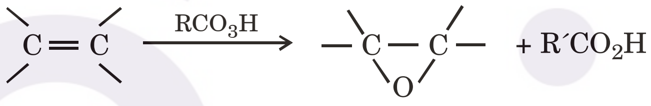
Note : **1.** Product is formed following Markownikov's rule.

2. Reaction proceeds via the formation of a cyclic mercurinium ion



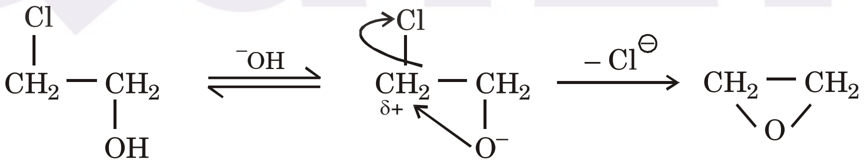
4. Preparation of epoxides

(a)



RCO_3H is peroxy acid.

(b) epoxides can also be prepared by internal S_N2 reaction of chlorohydrin



Example 28

(a) **Upon treatment with sulphuric acid, a mixture of ethyl and n-propyl alcohols yield a mixture of three ethers. What are they ?**

(b) **On the other hand, a mixture of tert-butyl alcohol and ethyl alcohol gives a good yield of a single ether. What ether is this likely to be ? How do you account for this good yield ?**

Solution :

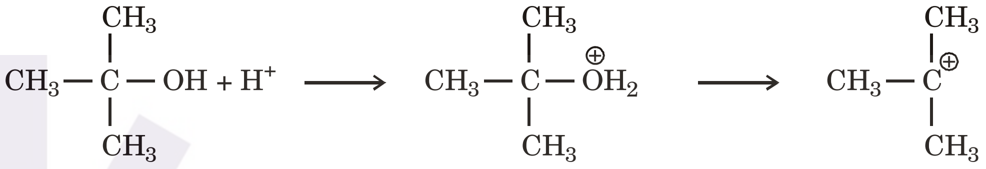
(a) CH_3CH_2OH (ethyl alcohol) and $CH_3CH_2CH_2OH$ (n-propyl alcohol) by dehydration make a mixture of three ethers since each alcohol is 1 and follow S_N2 reaction

$$CH_3CH_2OH + CH_3CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2OCH_2CH_3 + H_2O$$

$$CH_3CH_2CH_2OH + CH_3CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2CH_2OCH_2CH_2CH_3 + H_2O$$

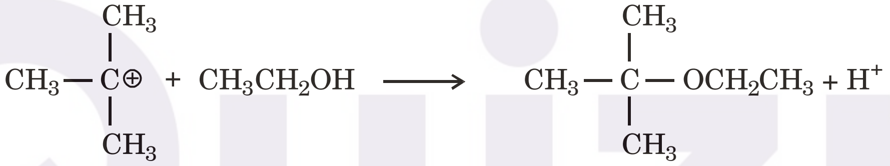
$$CH_3CH_2OH + CH_3CH_2CH_2OH \xrightarrow{H_2SO_4} CH_3CH_2CH_2OCH_2CH_3 + H_2O$$

(b)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + H^+ \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{O}H_2 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}$$

(3) most stable carbonium ion



$$CH_3-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}} + CH_3CH_2OH \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OCH_2CH_3 + H^+$$

Since protonated 3° alcohol (tert-butyl alcohol) can make most stable carbonium ion, hence this leads to the single ether in good quantity.

REACTIONS OF ETHERS

Ethers are relatively inert compounds and do not react with alkalies, reducing agent, oxidizing agents and reactive metals. Because of their inertness ethers are frequently used as solvents. They, however, undergo cleavage under acidic conditions.

1. Cleavage by acids

On reaction with conc. HBr or conc. HI, ethers undergo cleavage to form an alcohol or phenol and an alkyl halide.

$$C_2H_5-O-C_2H_5 + HX \longrightarrow C_2H_5X + C_2H_5OH$$

- The order of reactivity of halogen acids is

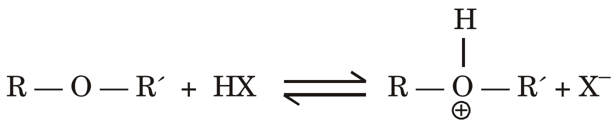
$$HI > HBr > HCl$$

- In case of excess acid, product formed is only alkyl halide

$$C_2H_5-O-C_2H_5 + \underset{\text{excess}}{2HX} \longrightarrow C_2H_5X + H_2O$$

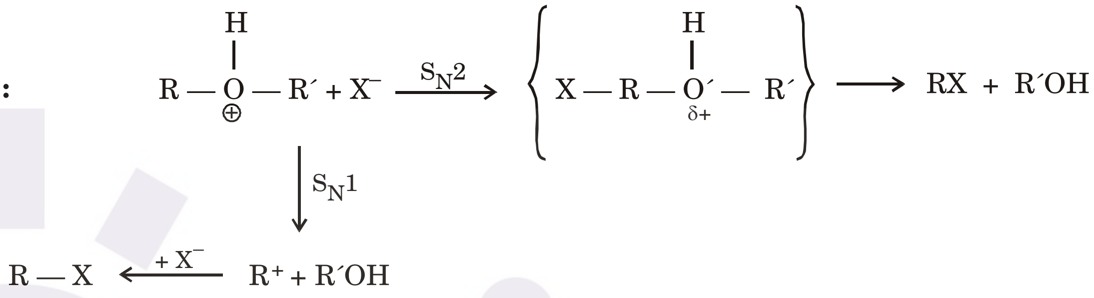
Mechanism :

Step I :



$$R-O-R' + HX \rightleftharpoons R-\underset{\oplus}{\overset{H}{\overset{|}{O}}}-R' + X^-$$

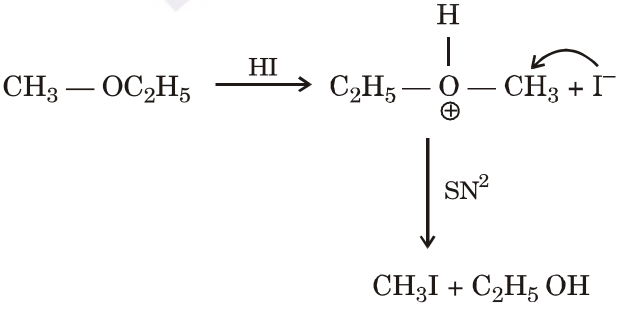
Setp II :



So, reaction can go by S_N1 or S_N2 depending upon the conditions employed and the structure of ether. When both the alkyl groups are methyl or 1 , it will follow S_N2 pathway and when atleast one of the alkyl group is 3 , it follows S_N1 pathway.

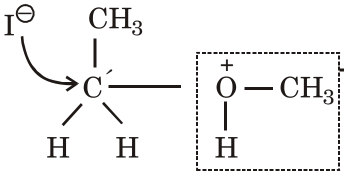
For example,

(a)



Here, $CH_3CH_2-\underset{\underset{H}{|}}{O}^{\oplus}$ is a good leaaving group and CH_3 is also not hindered. Therefore, CH_3I is formed.

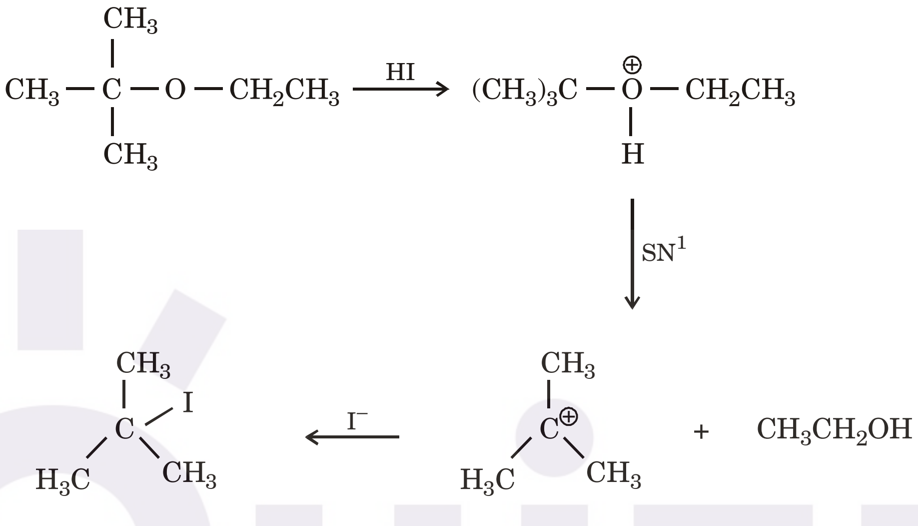
But



This is also a good leaving group but not as good as $C_2H_5O^{\oplus}$– H and C´ is also hindered

Hence, this product is not formed.

(b)



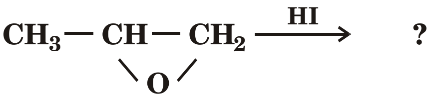
{stable carbocation}

Note : When the reaction follows S_N2 mechanism (R > R´) then I^- attacks R´ and forms R´I and ROH.

But, if S_N1 mechanism is followed than RI and R´OH is formed.

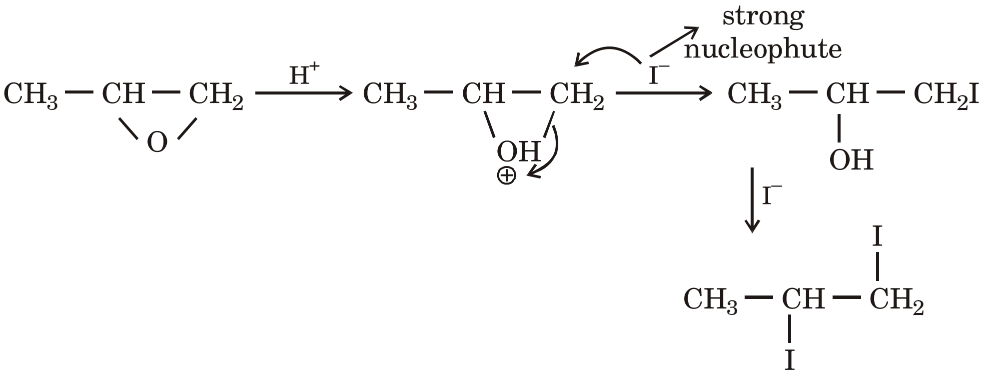
In acidic medium, in case of cleavage of ether, if strong nucleophile is used, then reaction takes place by S_N2 mechanism.

Example 29



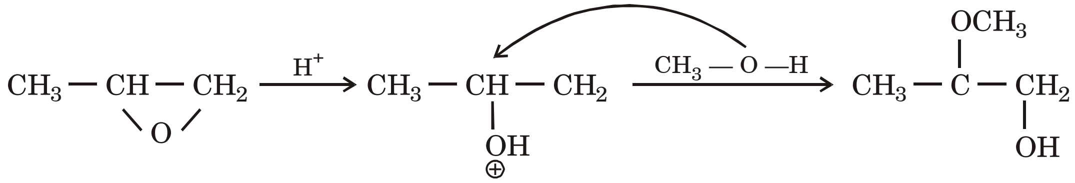
$$CH_3-CH-CH_2 \xrightarrow{HI} \ ?$$

Solution :



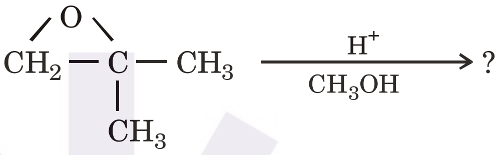
- Strong nucleophile will attack at less hundered carbon.

  But if we use CH_3OH instead of HI

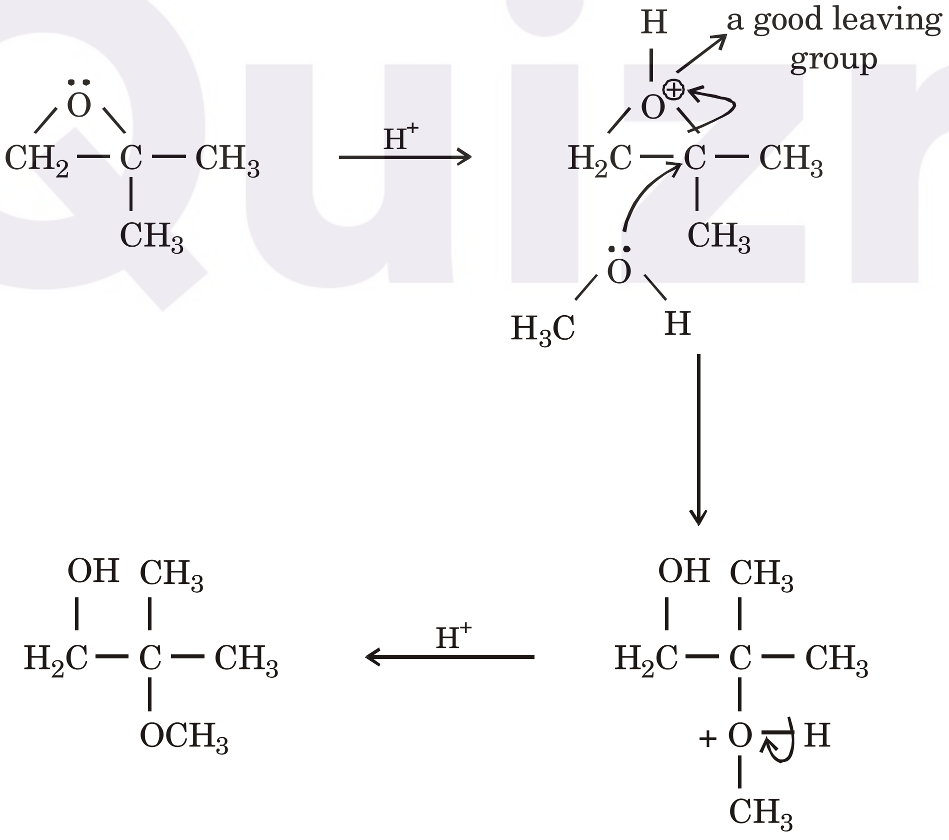


- In case of weak nucleophile, we break up the ring according to carbocation stability but actual carbocation is not formed.

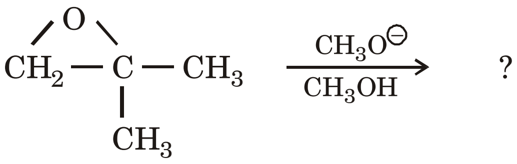
Example 30



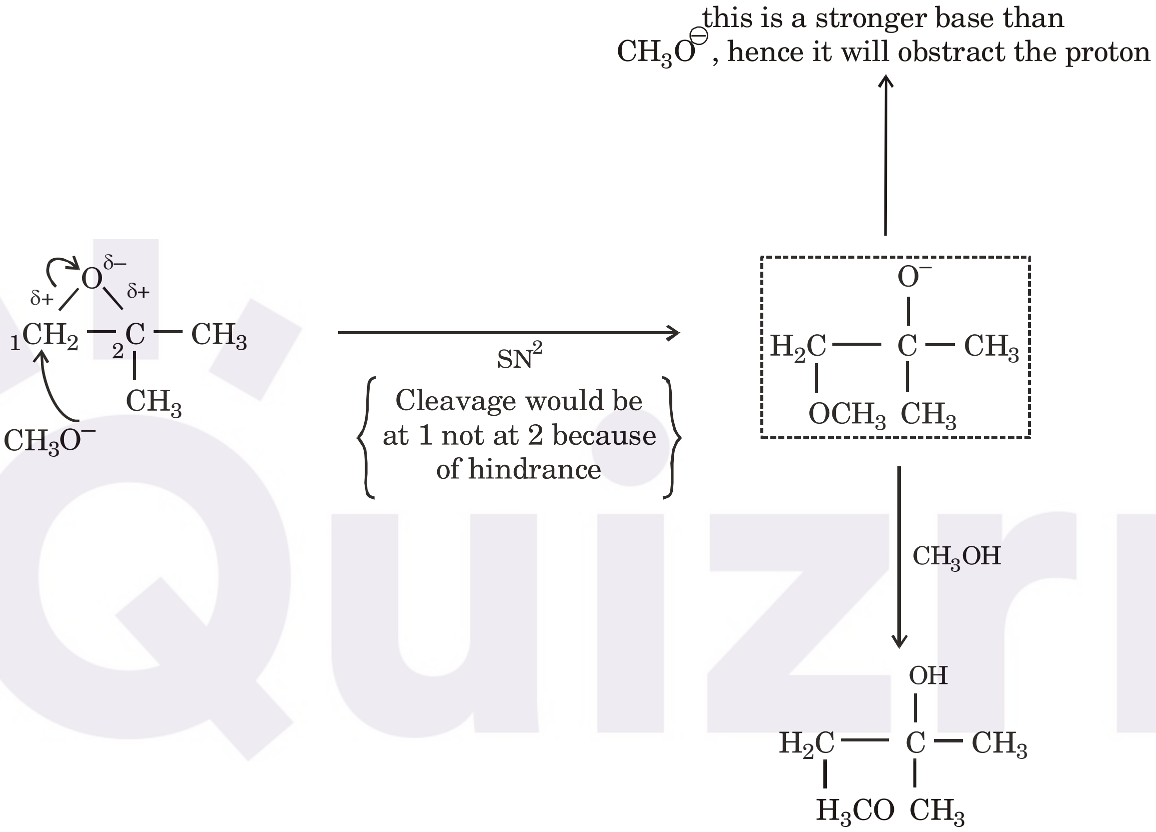
Solution :



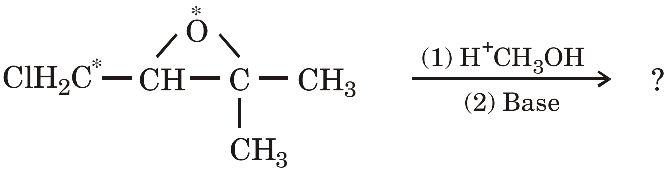
Example 31



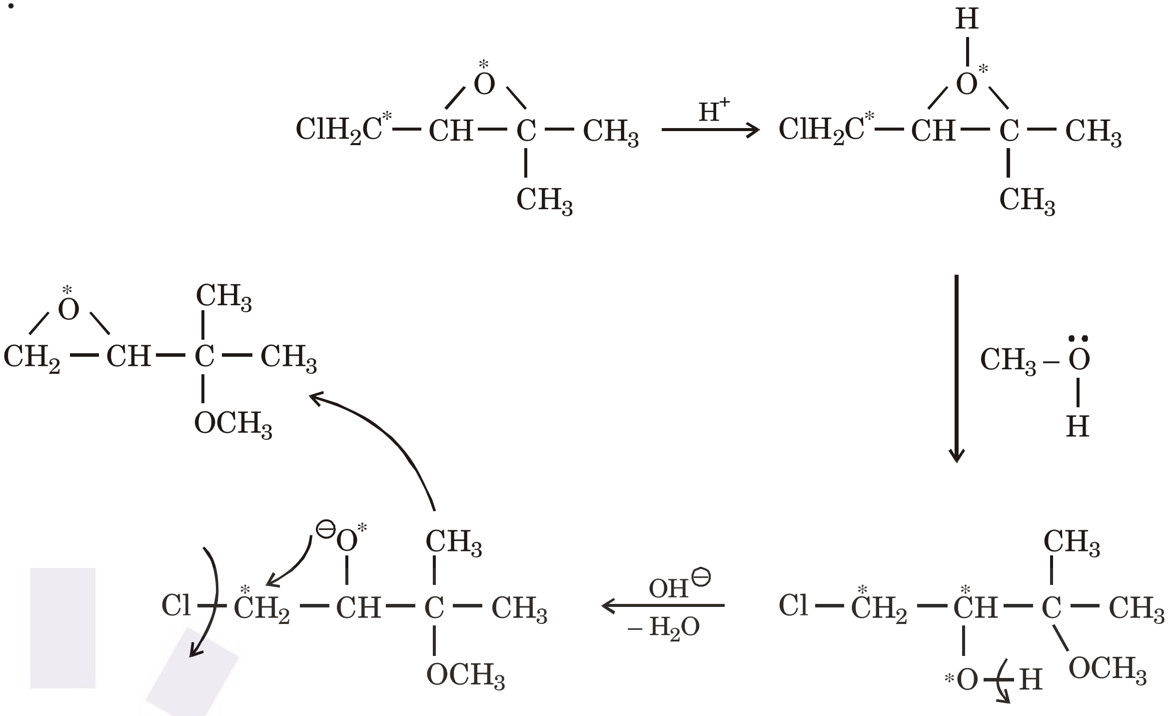
Solution :



Example 32



Solution :



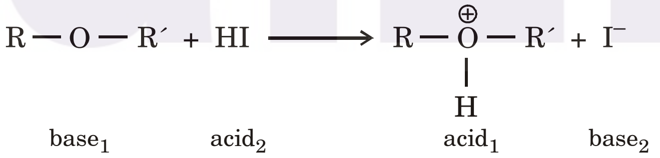
Example 33

(a) Give S_N2 and S_N1 mechanisms for the cleavage of ethers with HI.

(b) Why does S_N2 cleavage occur at a faster rate with HI than with HCl.

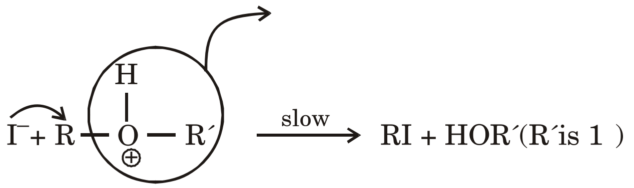
Solution :

(a) Step 1



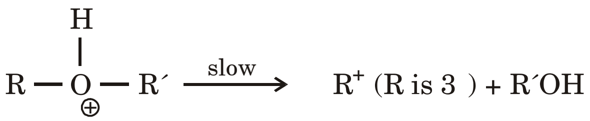
$$\underset{\text{base}_1}{R-O-R'} + \underset{\text{acid}_2}{HI} \longrightarrow \underset{\text{acid}_1}{R-\overset{\oplus}{\underset{H}{O}}-R'} + \underset{\text{base}_2}{I^-}$$

Step 2 for S_N2



$$I^- + R-\overset{H}{\underset{\oplus}{O}}-R' \xrightarrow{\text{slow}} RI + HOR'(R' \text{ is } 1\ )$$

Step 2 for S_N1



$$R-\overset{H}{\underset{\oplus}{O}}-R' \xrightarrow{\text{slow}} R^+ (R \text{ is } 3\ ) + R'OH$$

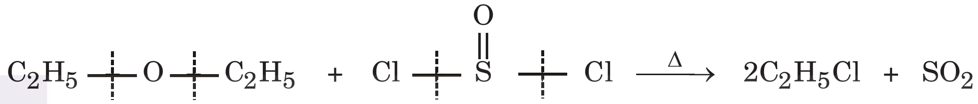
Setp 3 for S_N1 $R^+ + I^- \longrightarrow RI$

(b) The transfer of H^+ to ROR´ in step 1 is greater with HI, which is a stronger acid, than with HCl. Furthermore, in step 2, I^-, being a better nucleophile than Cl^-, reacts at a faster rate.

2. Reaction with PCl_5 /$SOCl_2$

Ethers on heating with PCl_5 or $SOCl_2$ undergoes cleavage to form alkyl chlorides.

$$C_2H_5 - O - C_2H_5 + Cl - PCl_3 - Cl \xrightarrow{\Delta} 2C_2H_5Cl + POCl_3$$

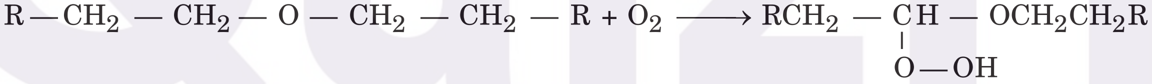


$$C_2H_5 - O - C_2H_5 + Cl - \overset{\overset{\displaystyle O}{\|}}{S} - Cl \xrightarrow{\Delta} 2C_2H_5Cl + SO_2$$

The cleavage by PCl_5 or $SOCl_2$ is and to distinguish metameric ethers as their cleavage.

3. Oxidation of Ether by Air

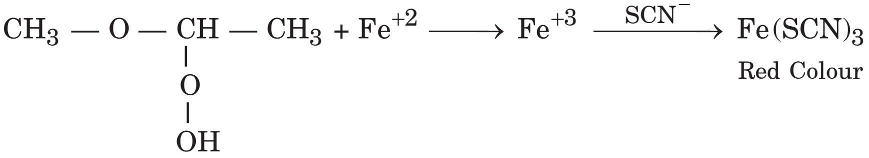
When ethers are exposed to oxygen for a long time they are oxidised to ether hydroperoxides (solid) which explodes on slightest heating or on rubbing.



$$R-CH_2-CH_2-O-CH_2-CH_2-R + O_2 \longrightarrow RCH_2-\underset{\displaystyle O-OH}{\underset{|}{C}H}-OCH_2CH_2R$$

Ethers are purified by extraction with excess of $FeSO_4$ solution, which reduces the –OOH gap to the non-explosive, innocuous — OH group.

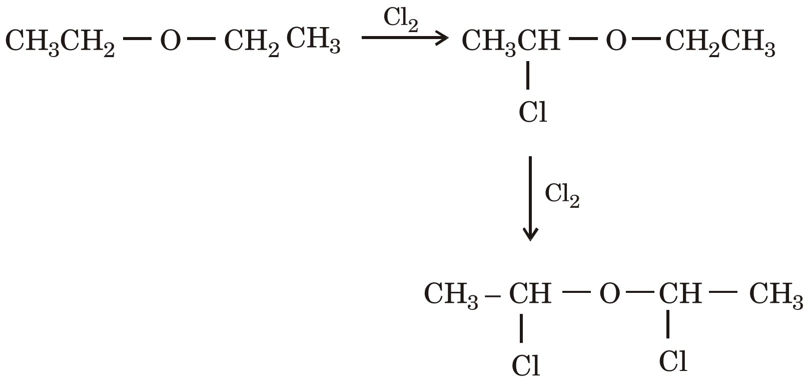
4. *Test of Peroxide ion*



$$CH_3-O-\underset{\underset{\displaystyle OH}{\underset{|}{\underset{\displaystyle O}{|}}}}{CH}-CH_3 + Fe^{+2} \longrightarrow Fe^{+3} \xrightarrow{SCN^-} \underset{\text{Red Colour}}{Fe(SCN)_3}$$

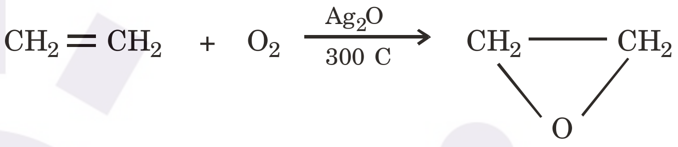
When ether hydroperoxide is reduced with Fe^{+2}, it oxidises Fe^{+2} to Fe^{+3} which can easily be detected by thiocyanide ion producing green colour.

5. *Halogenation of ether*

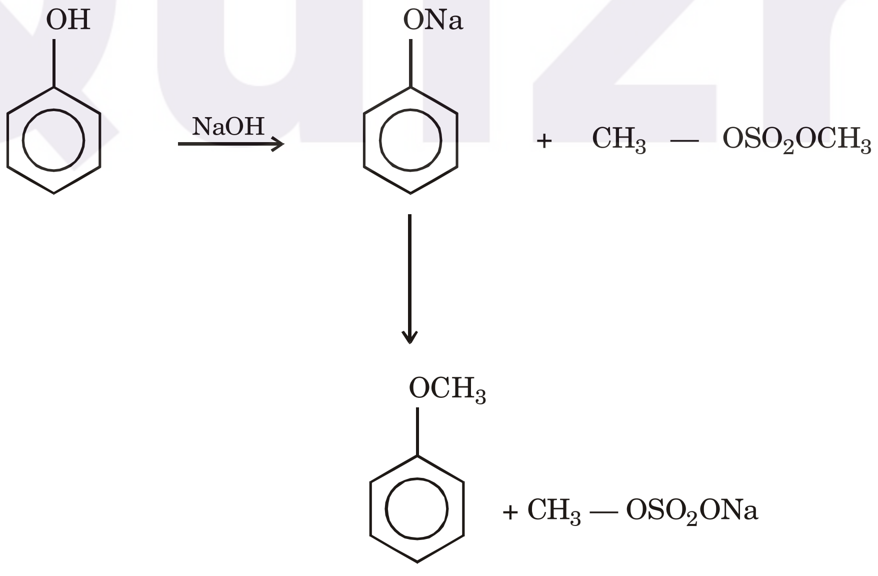


$$CH_3CH_2-O-CH_2CH_3 \xrightarrow{Cl_2} \underset{\displaystyle Cl}{CH_3\underset{|}{CH}}-O-CH_2CH_3 \xrightarrow{Cl_2} CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-O-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3$$

6. *Epoxidation*



7. *Formation of aryl ether*



(Anisole)

As discussed earlier, methyl sulphonates are better leaving group than halogens, hence are better for this kind of substitution.

Aryl halides cannot be used in the william son's synthesis because of their low reactivity towards nucleophilic substitution. There can be two combination of reactants for the preparation of alkyl aryl ether, but one can usually be ruled out.