ALCOHOLS, PHENOLS AND ETHERS

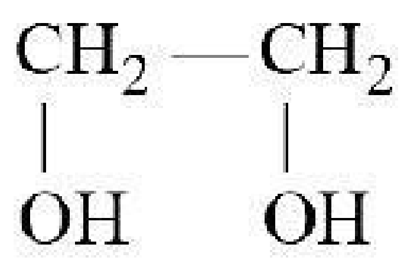
BASIC CONCEPTS

1. Alcohols and phenols are the compounds containing one or more hydroxyl groups (—OH). The alcohols contain the —OH group attached to the alkyl group whereas in phenols, the —OH group is attached to the aromatic ring.

Alcohols:

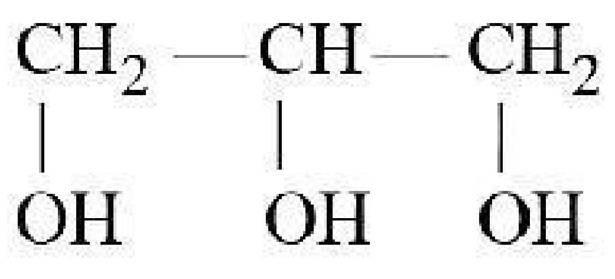
$CH_3—OH$

Methyl alcohol
(Monohydric)



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

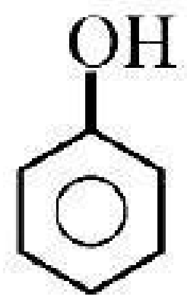
Ethylene glycol
(Dihydric)



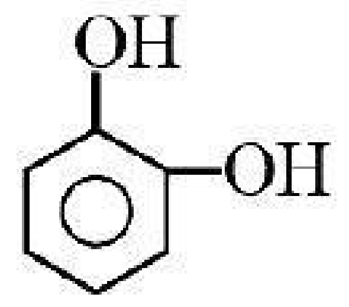
$\underset{OH}{CH_2}—\underset{OH}{CH}—\underset{OH}{CH_2}$

Glycerol
(Trihydric)

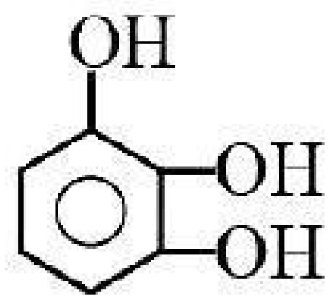
Phenols:



Phenol
(Monohydric)



Catechol
(Dihydric)



Pyrogallol
(Trihydric)

2. **Conversion of Alcohols**

[A] Ascent of Series

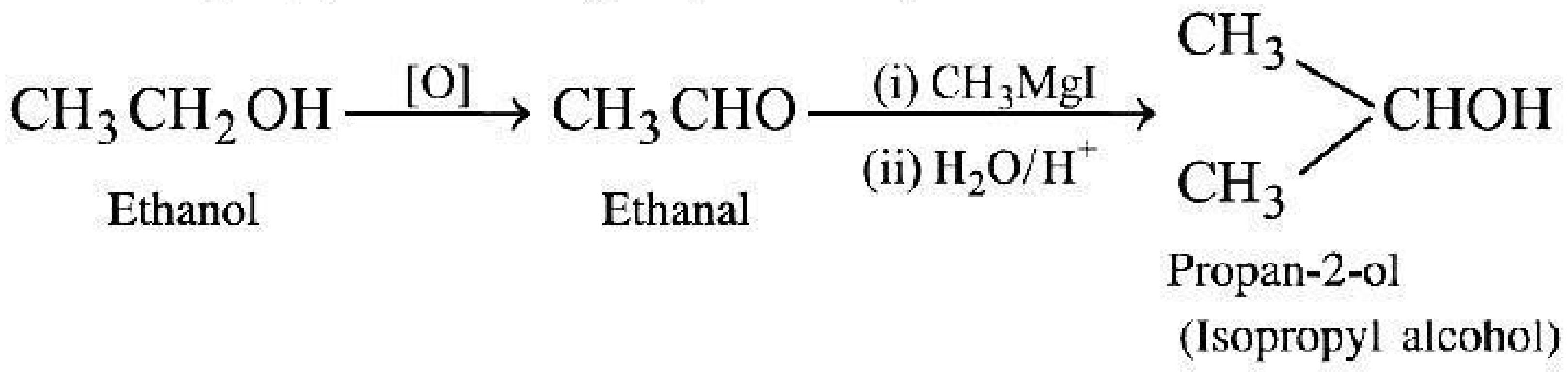
1. **Conversion of a Lower Primary Alcohol to a Higher Primary Alcohol.**

For example, methanol to ethanol

(a) $\underset{\text{Methanol}}{CH_3OH} \xrightarrow{P + I_2} \underset{\text{Iodomethane}}{CH_3I} \xrightarrow{KCN} \underset{\text{Methylcyanide}}{CH_3CN} \xrightarrow[LiAlH_4]{4H} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow{HNO_2} \underset{\text{Ethanol}}{CH_3CH_2OH}$

(b) $\underset{\text{Methanol}}{CH_3OH} \xrightarrow{P + I_2} \underset{\text{Iodomethane}}{CH_3I} \xrightarrow{Mg} \underset{\text{Methyl Magnesium Iodide}}{CH_3MgI} \xrightarrow{HCHO} \underset{\text{Addition Product}}{CH_3CH_2OMgI} \xrightarrow[H^+]{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH}$

2. **Conversion of a Primary Alcohol to a Higher Secondary Alcohol.** For example, conversion of ethanol to isopropyl alcohol (propan-2-ol)



$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{[O]} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_3MgI} \underset{\substack{\text{Propan-2-ol} \\ \text{(Isopropyl alcohol)}}}{\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOH}$$

3. **Conversion of a Secondary Alcohol to a Higher Tertiary Alcohol.**

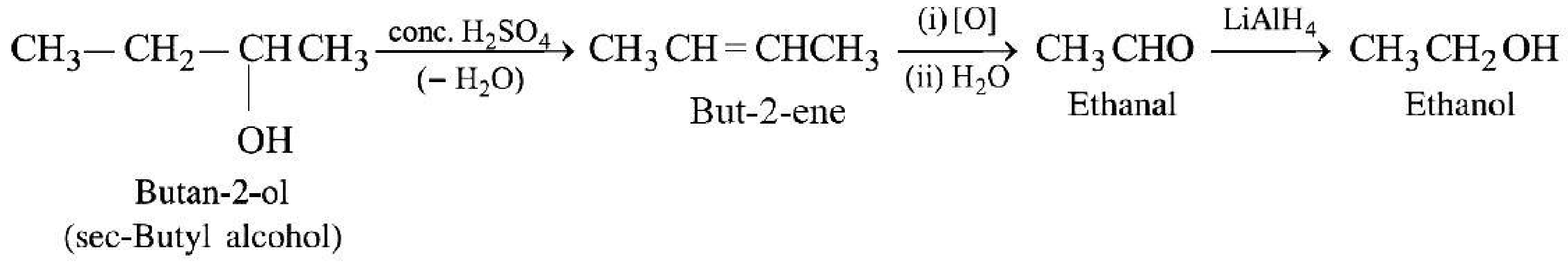
$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{[O]} \underset{\text{Acetone}}{(CH_3)_2C=O} \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CH_3MgI} \underset{\text{tert. Butyl alcohol}}{(CH_3)_3C—OH}$

[B] Descent of Series

1. **Conversion of a Higher Primary Alcohol to a lower Primary Alcohol.** For example, conversion of ethanol to methanol.

$$\begin{tikzcd}
\underset{\text{Ethanol}}{CH_3CH_2OH} \arrow[r, "{[O]}"] & \underset{\text{Acetaldehyde}}{CH_3CHO} \arrow[r, "{[O]}"] & \underset{\text{Acetic acid}}{CH_3COOH} \arrow[r, "NaOH", "CaO\ (-CO_2)"'] & \underset{\text{Methane}}{CH_4} \arrow[d, "Cl_2", "\text{U.V Light}"'] \\
 & & \underset{\text{Methanol}}{CH_3OH} & \underset{\text{Chloromethane}}{CH_3Cl} \arrow[l, "\text{Aq. KOH}"']
\end{tikzcd}$$

2. **Conversion of a Higher Secondary Alcohol into a Lower Primary Alcohol.** For example, the conversion of secondary butyl alcohol to ethanol.



$$\underset{\substack{\text{Butan-2-ol}\\\text{(sec-Butyl alcohol)}}}{CH_3-CH_2-\underset{OH}{\underset{|}{C}}HCH_3} \xrightarrow[(-H_2O)]{\text{conc. } H_2SO_4} \underset{\text{But-2-ene}}{CH_3CH=CHCH_3} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } [O]} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

3. **Conversion of a Tertiary Alcohol into a Lower Secondary Alcohol.** Example, conversion of tert. butanol to isopropanol.

$$\begin{tikzcd}
 & & \underset{\text{Acetone}}{(CH_3)_2CO} \arrow[r, "LiAlH_4"] & \underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \\
\underset{\text{tert. Butyl alcohol}}{(CH_3)_3C-OH} \arrow[r, "\text{conc. } H_2SO_4", "(-H_2O)"'] & \underset{\text{Isobutene}}{(CH_3)_2C=CH_2} \arrow[ur, "\text{(i) } [O]"] \arrow[dr, "\text{(ii) } H_2O"'] & & \\
 & & \underset{\substack{\text{Formaldehyde}\\\text{(Methanal)}}}{HCHO} \arrow[r, "LiAlH_4"] & \underset{\text{Methanol}}{CH_3OH}
\end{tikzcd}$$

[C] Interconversion of Primary, Secondary and Tertiary Alcohols

1. **Primary Alcohol into Secondary Alcohol.** Example : conversion of *n*-propanol to isopropanol.

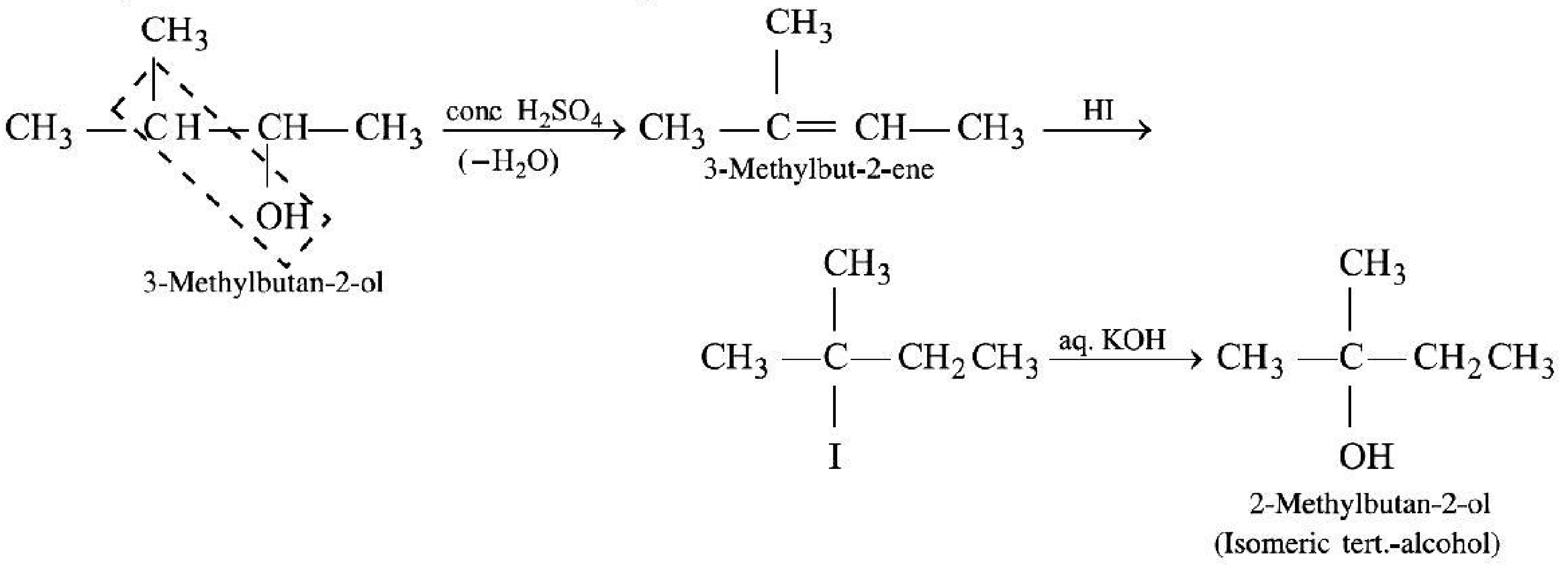
$$\begin{tikzcd}
\underset{n\text{-propanol}}{CH_3CH_2CH_2OH} \arrow[r, "\text{Conc. } H_2SO_4", "-H_2O"'] \arrow[d, "PCl_5"] & \underset{\text{Propene}}{CH_3-CH=CH_2} \arrow[d, "HI"] \\
CH_3CH_2CH_2Cl \arrow[ur, "\text{Alcoholic KOH}", "-HCl"'] & CH_3CHICH_3 \arrow[d, "\text{Aq KOH}"] \\
 & CH_3CH(OH)CH_3
\end{tikzcd}$$

2. **Secondary Alcohol into Tertiary Alcohol.** Example : Conversion of isopropyl alcohol into tertiary butyl alcohol.

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{[O]} \underset{\text{Acetone}}{(CH_3)_2C=O} \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CH_3MgI} \underset{\text{tert. Butyl alcohol}}{(CH_3)_3C-OH}$$

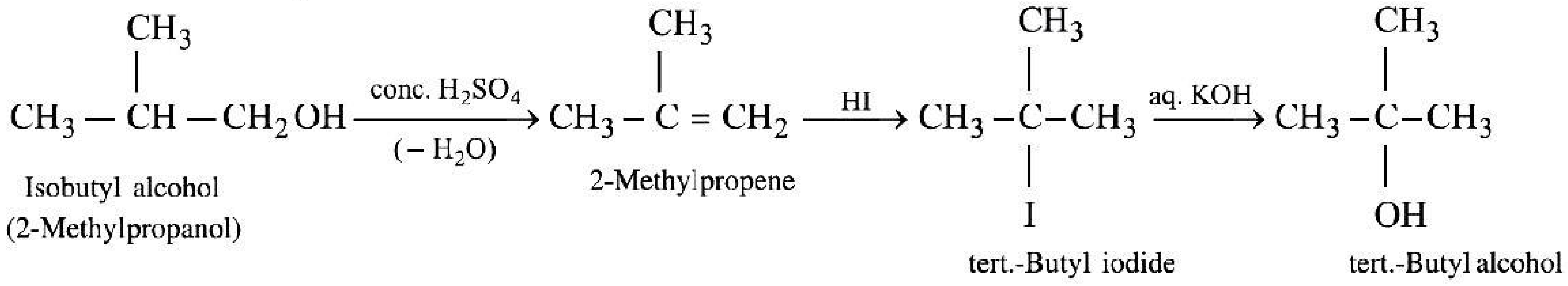
[D] Interconversion of Isomeric Alcohols

1. **Conversion of a Secondary Alcohol to Isomeric Tertiary Alcohol.** Example, conversion of 3-methylbutan-2-ol into isomeric 2-methylbutan-2-ol.



$$\underset{\text{3-Methylbutan-2-ol}}{CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3} \xrightarrow[(-H_2O)]{\text{conc } H_2SO_4} \underset{\text{3-Methylbut-2-ene}}{CH_3-\overset{CH_3}{C}=CH-CH_3} \xrightarrow{HI} CH_3-\underset{I}{\overset{CH_3}{C}}-CH_2CH_3 \xrightarrow{\text{aq. KOH}} \underset{\text{(Isomeric tert.-alcohol)}}{\underset{\text{2-Methylbutan-2-ol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CH_3}}$$

2. **Conversion of a Primary Alcohol into Isomeric Tertiary Alcohol.** Example, conversion of isobutyl alcohol to tert. butyl alcohol.



$$\underset{\text{(2-Methylpropanol)}}{\underset{\text{Isobutyl alcohol}}{CH_3-\overset{CH_3}{CH}-CH_2OH}} \xrightarrow[(-H_2O)]{\text{conc. } H_2SO_4} \underset{\text{2-Methylpropene}}{CH_3-\overset{CH_3}{C}=CH_2} \xrightarrow{HI} \underset{\text{tert.-Butyl iodide}}{CH_3-\underset{I}{\overset{CH_3}{C}}-CH_3} \xrightarrow{\text{aq. KOH}} \underset{\text{tert.-Butyl alcohol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3}$$

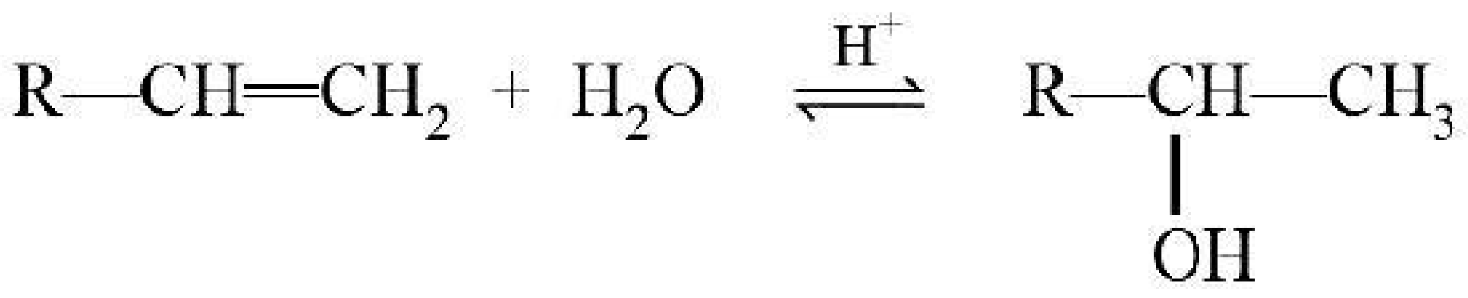
3. Methods of Preparation

Alcohols are prepared by following methods:

(*a*) From alkenes

(*i*) By acid catalysed hydration:

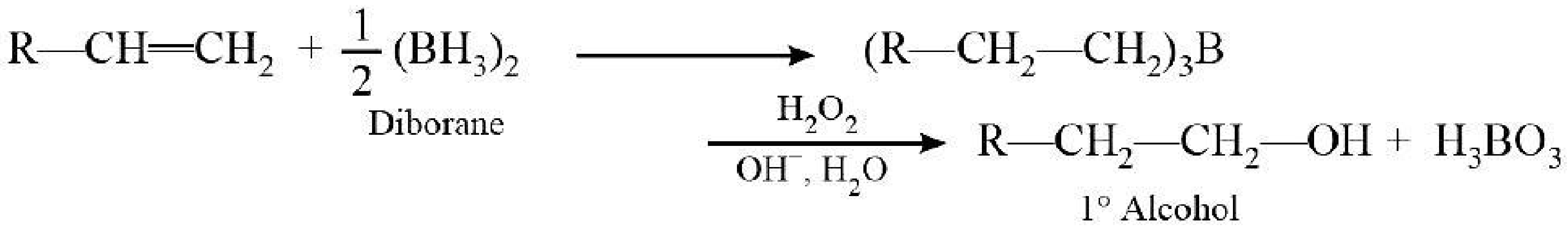
Addition occurs according to Markovnikov's rule.



$$R-CH=CH_2 + H_2O \overset{H^+}{\rightleftharpoons} R-\underset{OH}{CH}-CH_3$$

(*ii*) By hydroboration oxidation:

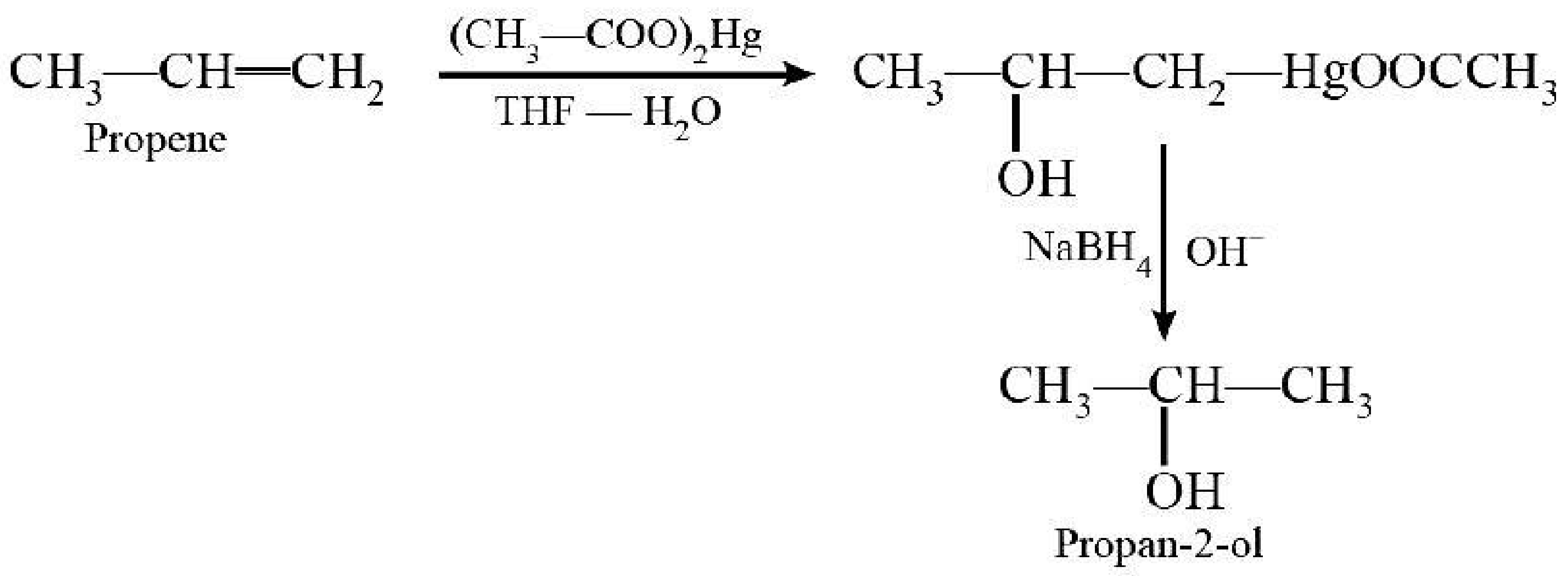
Addition occurs in accordance with anti-Markovnikov's rule.



$$R-CH=CH_2 + \frac{1}{2}\underset{\text{Diborane}}{(BH_3)_2} \longrightarrow (R-CH_2-CH_2)_3B \xrightarrow[OH^-,\ H_2O]{H_2O_2} \underset{1^\circ\ \text{Alcohol}}{R-CH_2-CH_2-OH} + H_3BO_3$$

(*iii*) By oxymercuration-demercuration:

Addition occurs according to Markovnikov's rule.

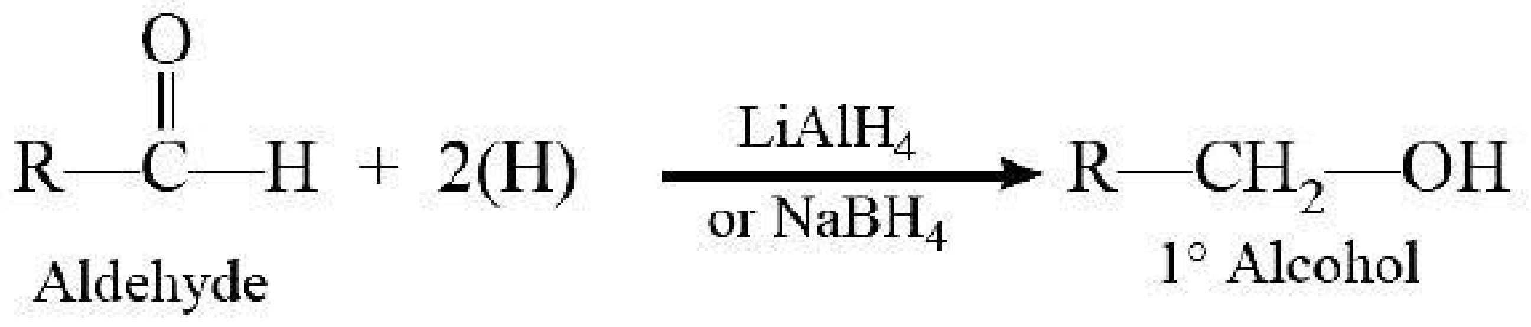


$$\underset{\text{Propene}}{CH_3-CH=CH_2} \xrightarrow[THF-H_2O]{(CH_3-COO)_2Hg} CH_3-\underset{OH}{CH}-CH_2-HgOOCCH_3 \xrightarrow{NaBH_4,\ OH^-} \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{CH}-CH_3}$$

(*b*) From carbonyl compounds

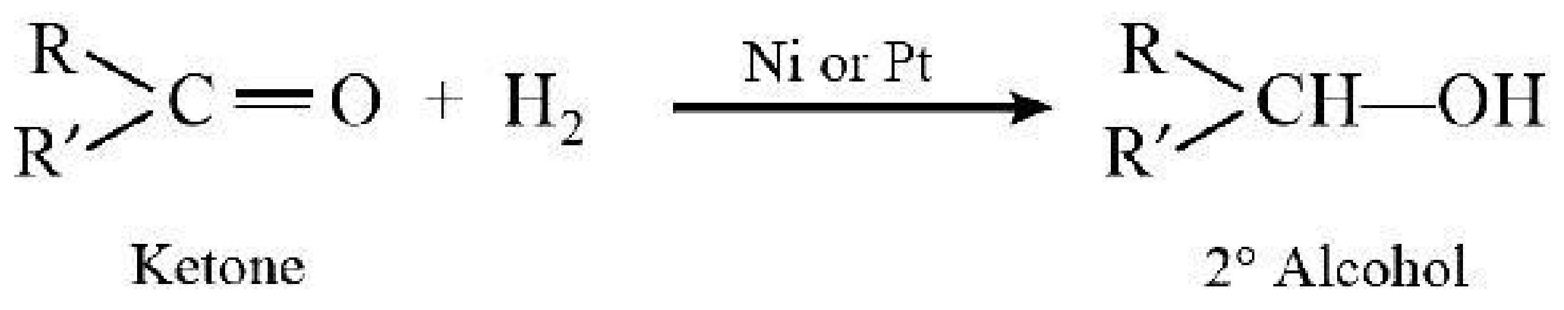
(*i*) By reduction of aldehydes and ketones:

Common reducing agents used are lithium aluminium hydride ($LiAlH_4$), sodium borohydride ($NaBH_4$), H_2 in the presence of Ni or Pt. Aldehydes on reduction give 1° alcohols whereas ketones on reduction give 2° alcohols.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + 2(H) \xrightarrow[\text{or } NaBH_4]{LiAlH_4} R-CH_2-OH$$

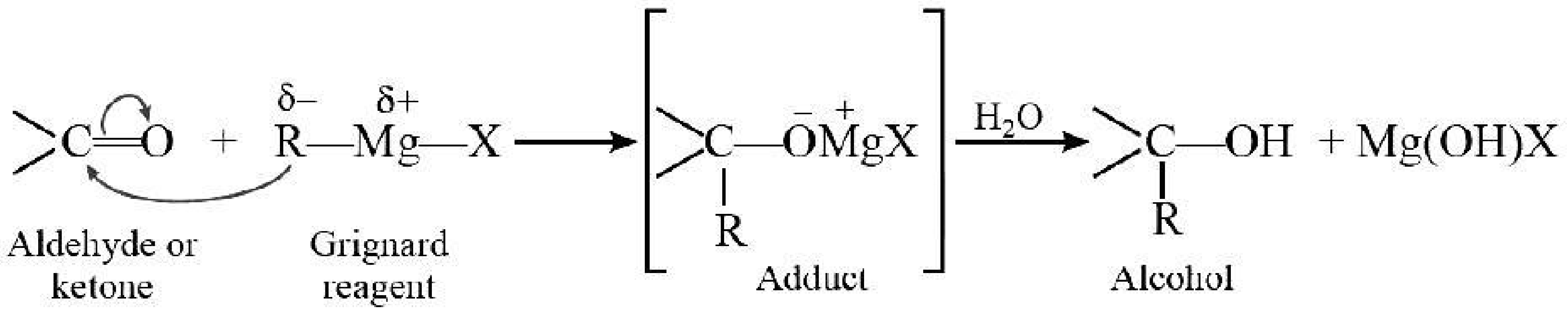
Aldehyde → 1° Alcohol



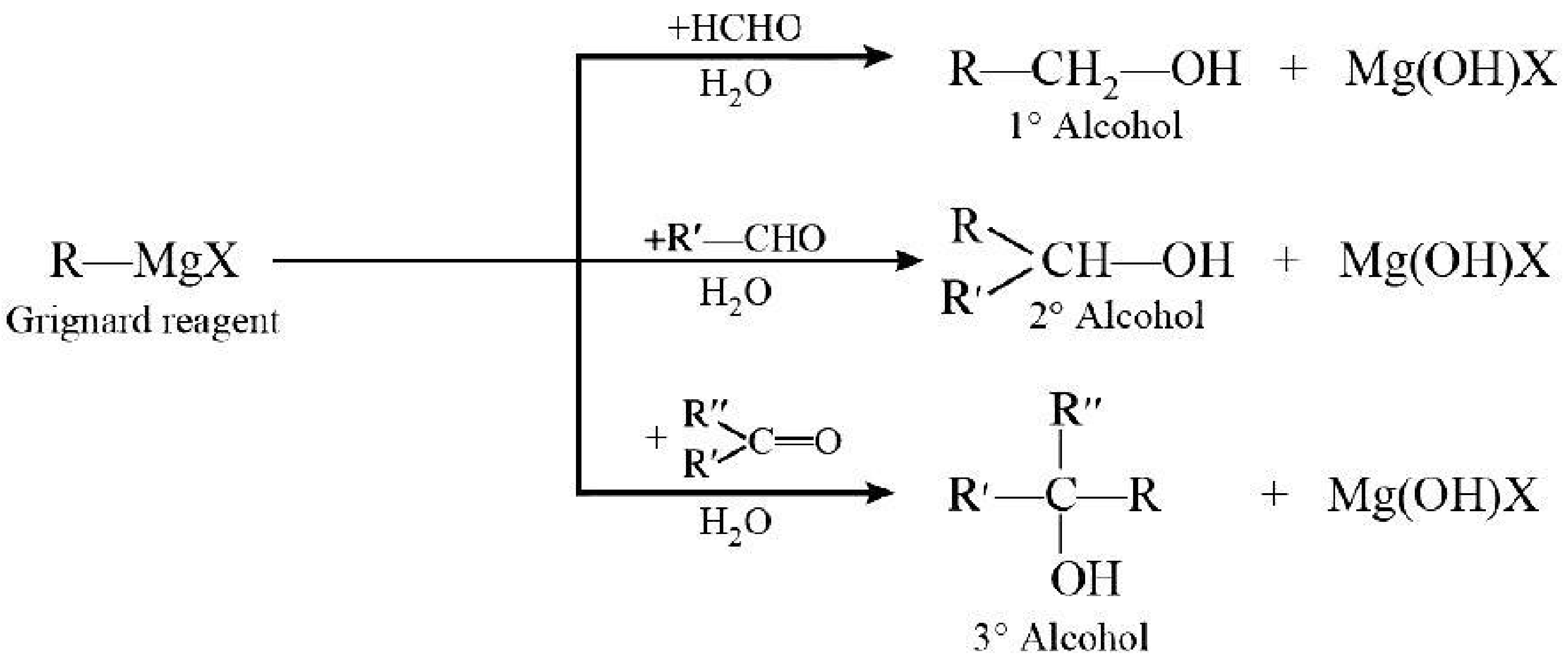
$$RR'C=O + H_2 \xrightarrow{\text{Ni or Pt}} RR'CH-OH$$

Ketone → 2° Alcohol

(*ii*) From Grignard's reagents



The reaction of Grignard's reagents with formaldehyde produces a primary alcohol, with other aldehydes it produces secondary alcohols and tertiary alcohols with ketones.



(*iii*) By reduction of carboxylic acids and esters:

$$\underset{\text{Carboxylic acid}}{R-COOH} \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} \underset{1^\circ\text{Alcohol}}{R-CH_2-OH}$$

$$\underset{\text{Ester}}{R-COOR'} \xrightarrow{H_2/Pd} \underset{1^\circ\text{Alcohol}}{R-CH_2-OH} + R'-OH$$

(*c*) By the hydrolysis of haloalkanes

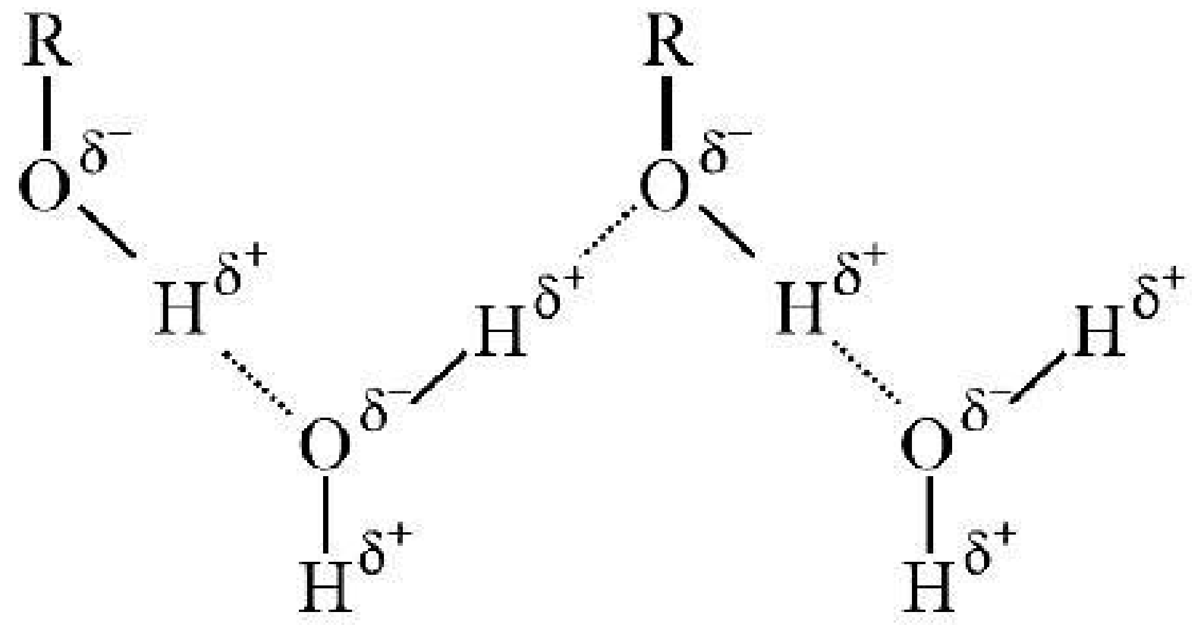
$$RX + KOH(aq) \longrightarrow R-OH + KX$$

On hydrolysis with aqueous KOH, primary alkyl halides give good yield of primary alcohols; secondary alkyl halides give a mixture of alcohol and alkene while tertiary alkyl halides mainly give alkenes.

4. Physical Properties of Alcohols:

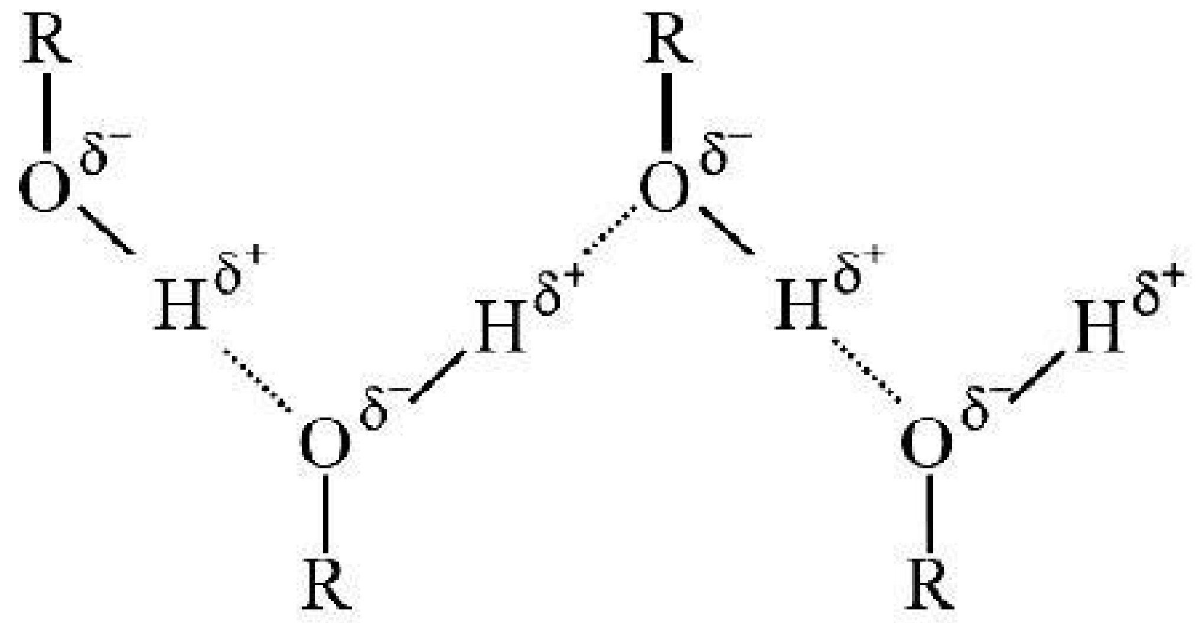
(*a*) The lower members of alcohols are colourless, volatile liquids with a characteristic alcoholic smell and burning taste whereas higher alcohols are odourless and tasteless. Higher alcohols having 12 or more carbon atoms are colourless waxy solids.

(*b*) **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 ether, benzene, etc. The solubility of lower alcohols in water is due to their ability to form hydrogen bonds with water molecules.



The solubility of alcohols in water decreases with increase in molecular mass because with increase in molecular mass the non-polar alkyl group becomes predominant and masks the effect of polar —OH group. In addition, among the isomeric alcohols the solubility increases with branching of chain. It is because the surface area of non-polar part in the molecule decreases, thus enhancing the solubility.

(*c*) **Boiling points:** Boiling points of alcohols are much higher than those of alkanes, haloalkanes or ethers of comparable molecular masses. This is because in alcohols strong intermolecular hydrogen bonding exists due to which a large amount of energy is required to break these bonds.



Among isomeric alcohols, the boiling point decreases with increase in branching in the alkyl group. For isomeric alcohols, the boiling points generally follow the order:

Primary alcohol > secondary alcohol > tertiary alcohol.

5. Chemical Properties of Alcohols:

The reactions of alcohols can be classified into three types:

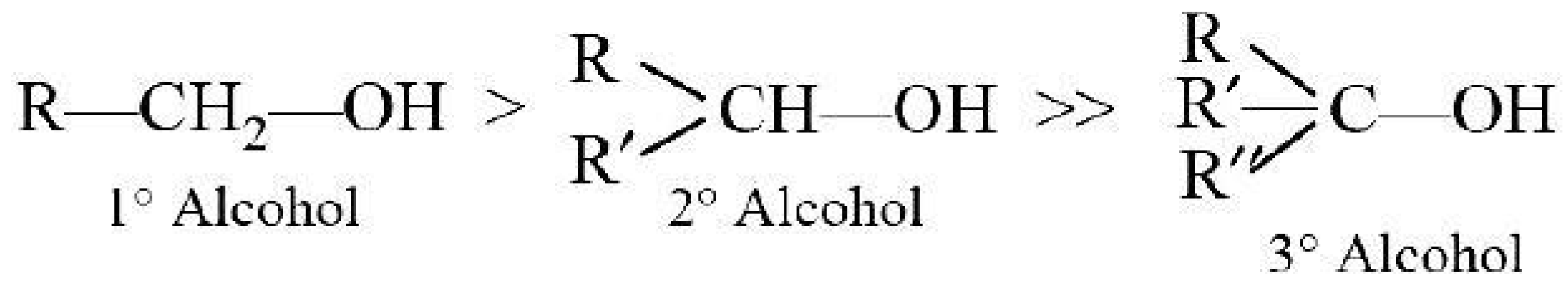
(*a*) Reactions involving the cleavage of oxygen–hydrogen bond.

(*b*) Reactions involving the cleavage of carbon–oxygen bond.

(*c*) Reactions involving both the alkyl as well as the hydroxyl group.

(*a*) Reactions involving cleavage of oxygen–hydrogen (O—H) bond

Acidity of alcohols: The acidic character of alcohols is due to the polar nature of O—H bond. An electron releasing group (alkyl group) increases electron density on oxygen tending to decrease the polarity of O—H bond. This decreases the acid strength. For this reason, the acid strength of alcohols decreases in the following order:



$$\underset{1^\circ\text{ Alcohol}}{R{-}CH_2{-}OH} > \underset{2^\circ\text{ Alcohol}}{RR'CH{-}OH} \gg \underset{3^\circ\text{ Alcohol}}{RR'R''C{-}OH}$$

(*i*) Reaction with metals:

$$2R{-}O{-}H + 2Na \longrightarrow \underset{\text{Sodium alkoxide}}{2R{-}\overset{-}{O}\overset{+}{Na}} + H_2$$

$$\underset{\text{Ethyl alcohol}}{CH_3{-}CH_2{-}OH} + Na \longrightarrow \underset{\text{Sodium ethoxide}}{CH_3{-}CH_2{-}\overset{-}{O}\overset{+}{Na}} + \frac{1}{2}H_2$$

$$\underset{3^\circ\text{ Butyl alcohol}}{6(CH_3)_3{-}C{-}OH} + 2Al \longrightarrow \underset{\text{Aluminium tert -butoxide}}{2((CH_3)_3{-}C{-}O)_3Al} + 3H_2$$

(*ii*) Esterification:

$$\underset{\text{Carboxylic acid}}{R{-}COOH} + \underset{\text{Alcohol}}{R'{-}OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R{-}COOR'} + H_2O$$

$$\underset{\text{Acid anhydride}}{(R{-}CO)_2O} + R'{-}OH \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R{-}COOR'} + R{-}COOH$$

$$\underset{\text{Acyl chloride}}{R{-}COCl} + R'{-}OH \xrightarrow{\text{Pyridine}} \underset{\text{Ester}}{R{-}COOR'} + HCl$$

(*b*) Reactions involving cleavage of carbon–oxygen (C—O) bond

In such type of reactions, the order of reactivity of alcohols is

3°Alcohol > 2°Alcohol > 1°Alcohol

(*i*) Reaction with hydrogen halides:

$$\underset{\text{Alcohol}}{R{-}OH} + H{-}X \longrightarrow \underset{\text{Alkyl halide}}{R{-}X} + H_2O$$

$$CH_3{-}CH_2{-}OH + H{-}Cl \xrightarrow{\text{Anhyd. } ZnCl_2} CH_3{-}CH_2{-}Cl + H_2O$$

(*ii*) Reaction with phosphorus halides:

$$R{-}OH + PCl_5 \longrightarrow R{-}Cl + POCl_3 + HCl$$

$$3R{-}OH + PCl_3 \longrightarrow 3R{-}Cl + H_3PO_3$$

$$3R{-}OH + PBr_3 \xrightarrow{\text{from } (P \,\&\, Br_2)} 3R{-}Br + H_3PO_3$$

$$3R{-}OH + PI_3 \xrightarrow{\text{from } (P \,\&\, I_2)} 3R{-}I + H_3PO_3$$

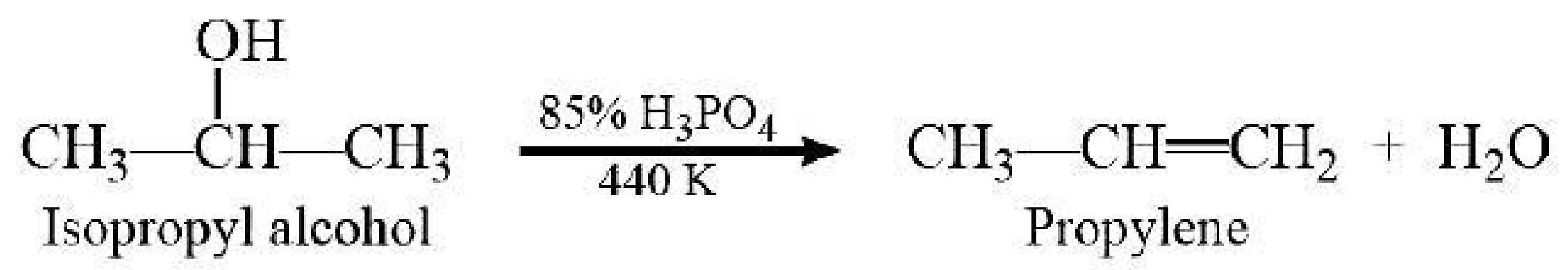
$$R{-}OH + SOCl_2 \longrightarrow R{-}Cl + SO_2\uparrow + HCl\uparrow$$

(*c*) Reactions involving both the alkyl as well as the hydroxyl group

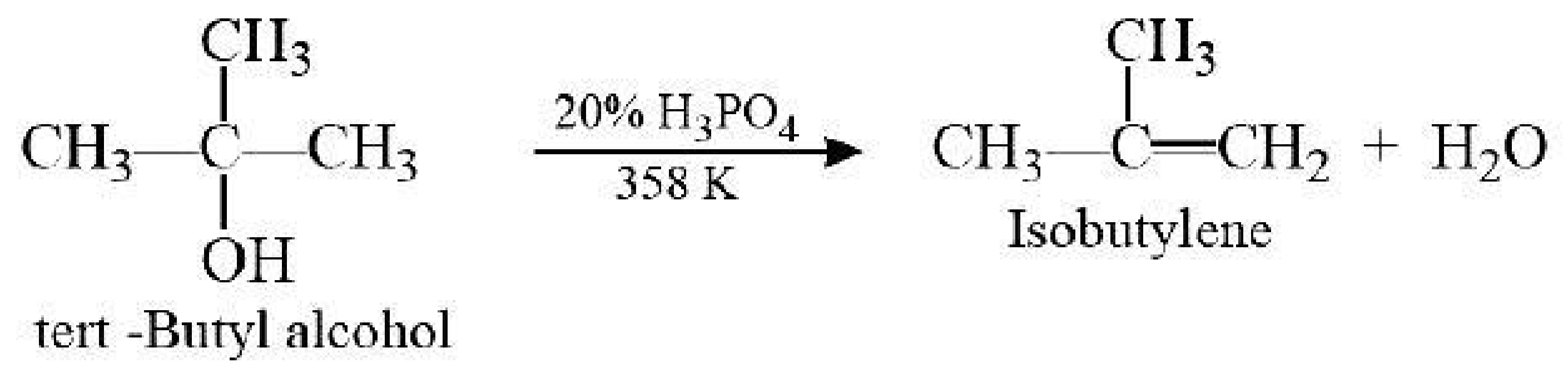
(*i*) Dehydration: The ease of dehydration follows the following order:

3° Alcohol > 2° Alcohol > 1° Alcohol

$$\underset{\text{Ethyl alcohol}}{CH_3{-}CH_2{-}OH} \xrightarrow[443\text{ K}]{H_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2} + H_2O$$

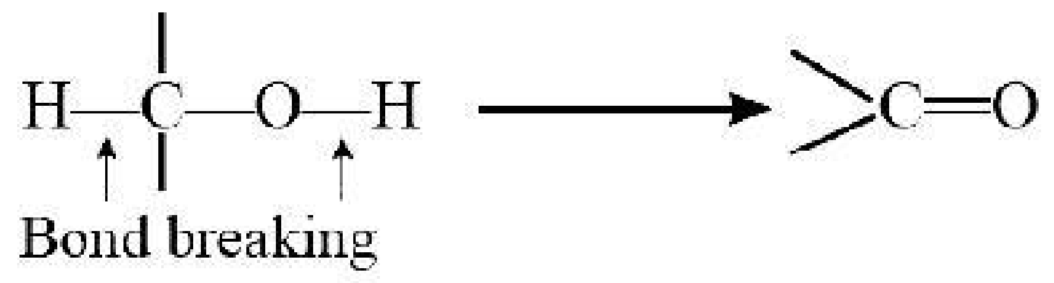


$$\underset{\text{Isopropyl alcohol}}{CH_3{-}\overset{\displaystyle OH}{\overset{|}{C}H}{-}CH_3} \xrightarrow[440\text{ K}]{85\%\ H_3PO_4} \underset{\text{Propylene}}{CH_3{-}CH{=}CH_2} + H_2O$$



$$\underset{\text{tert -Butyl alcohol}}{CH_3{-}\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}CH_3} \xrightarrow[358\text{ K}]{20\%\ H_3PO_4} \underset{\text{Isobutylene}}{CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2} + H_2O$$

(*ii*) Oxidation: Oxidation of alcohols involves the formation of a carbon–oxygen double bond with the cleavage of an O—H and C—H bond.



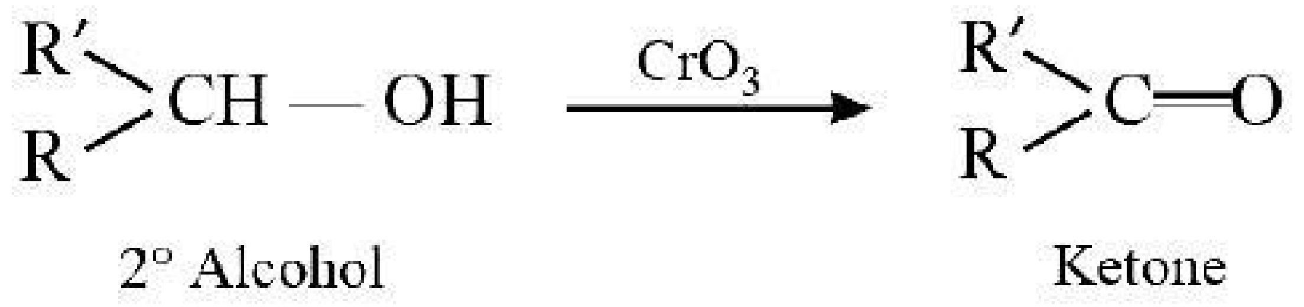
Bond breaking

1° alcohols on oxidation give aldehydes which on further oxidation give carboxylic acids with the same number of carbon atoms.

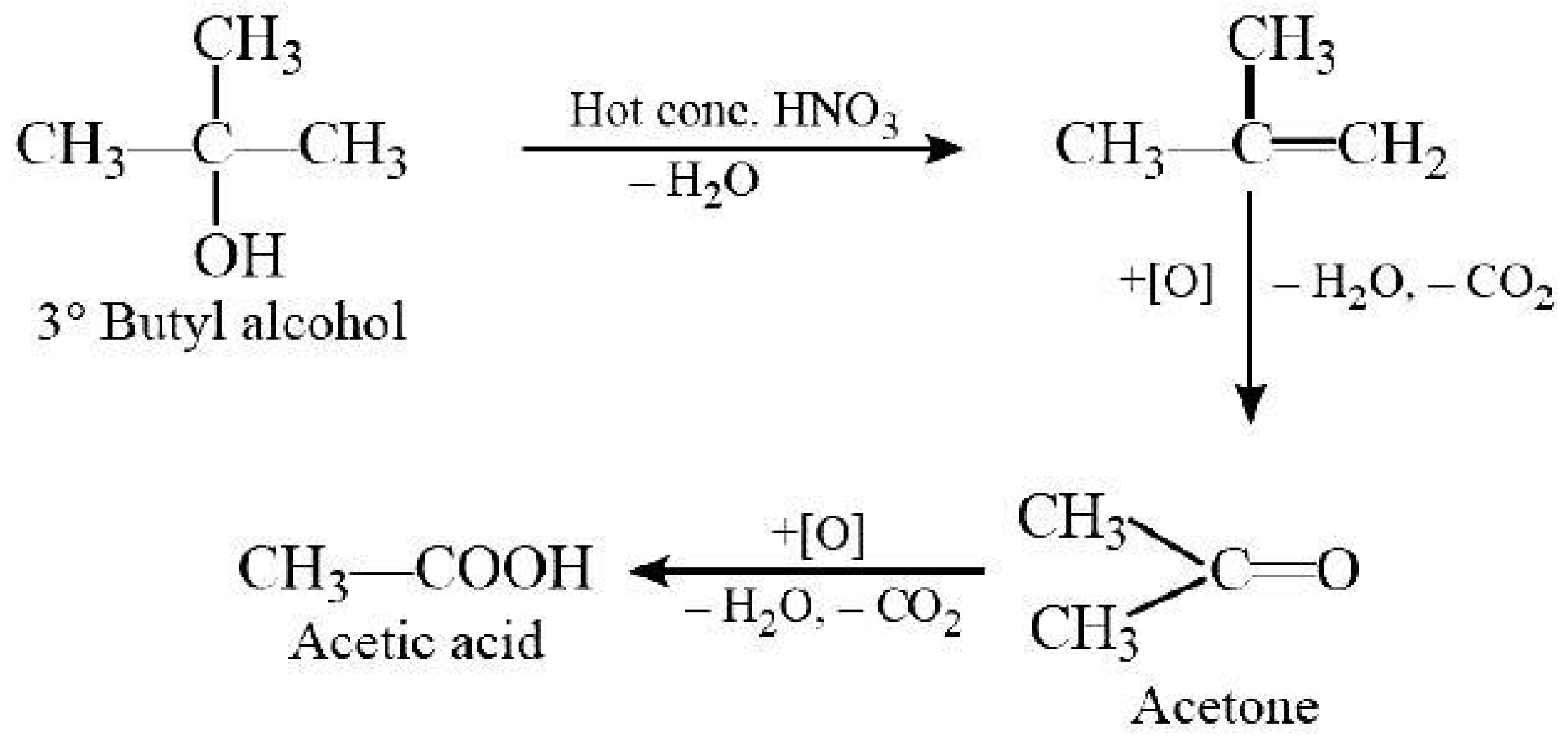
$$\underset{1^\circ\text{ Alcohol}}{R{-}CH_2{-}OH} + [O] \xrightarrow[\substack{\text{or alk. } KMnO_4\\ -H_2O}]{K_2Cr_2O_7/H_2SO_4} \underset{\text{Aldehyde}}{R{-}CHO} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{R{-}COOH}$$

$$\underset{\text{But -2-enol}}{CH_3{-}CH{=}CH{-}CH_2{-}OH} \xrightarrow{PCC} \underset{\text{But-2-enal}}{CH_3{-}CH{=}CH{-}CHO}$$

2° Alcohols are oxidised to ketones by CrO_3.



3° alcohols do not undergo oxidation reaction as they do not have α-hydrogens. However, when oxidation is carried under strong reaction conditions and elevated temperature, they undergo oxidation with the cleavage of C—C bond.

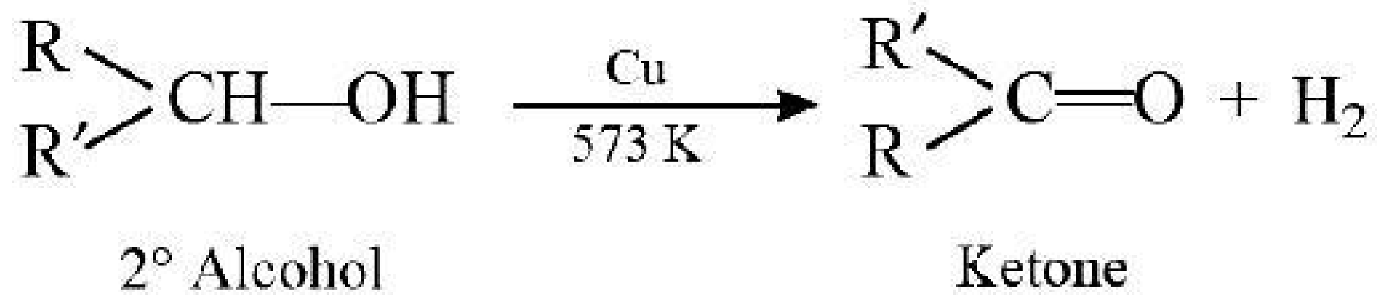


(*iii*) Dehydrogenation

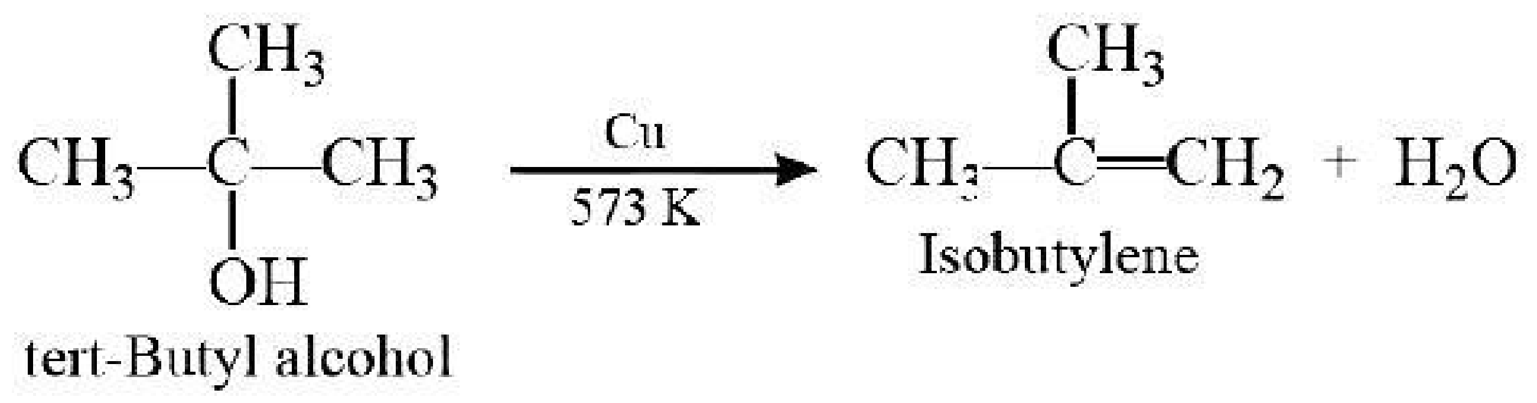
Primary alcohols are dehydrogenated to aldehydes.

$$\underset{1^\circ\ \text{Alcohol}}{R{-}CH_2{-}OH} \xrightarrow[573\ K]{Cu} \underset{\text{Aldehyde}}{R{-}CHO} + H_2$$

Secondary alcohols are dehydrogenated to ketones.

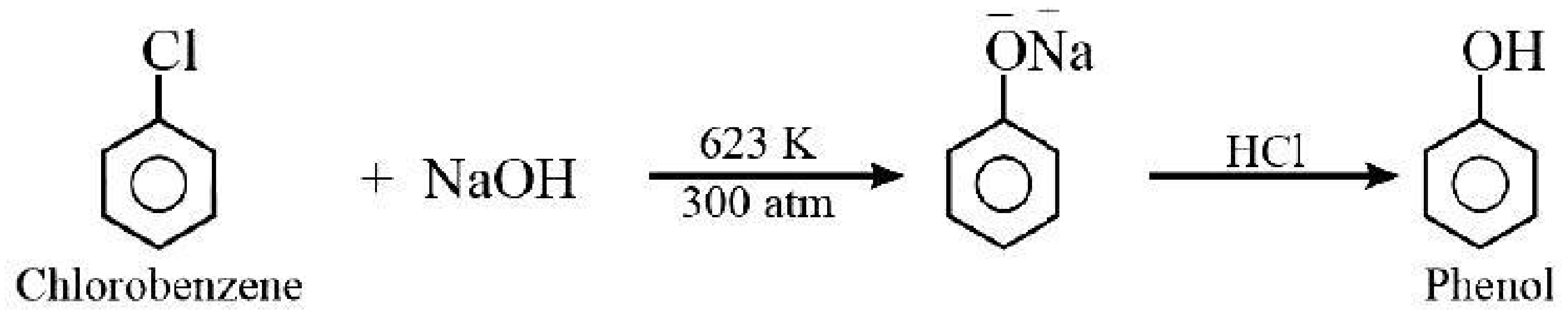


Tertiary alcohols undergo dehydration to give alkenes.

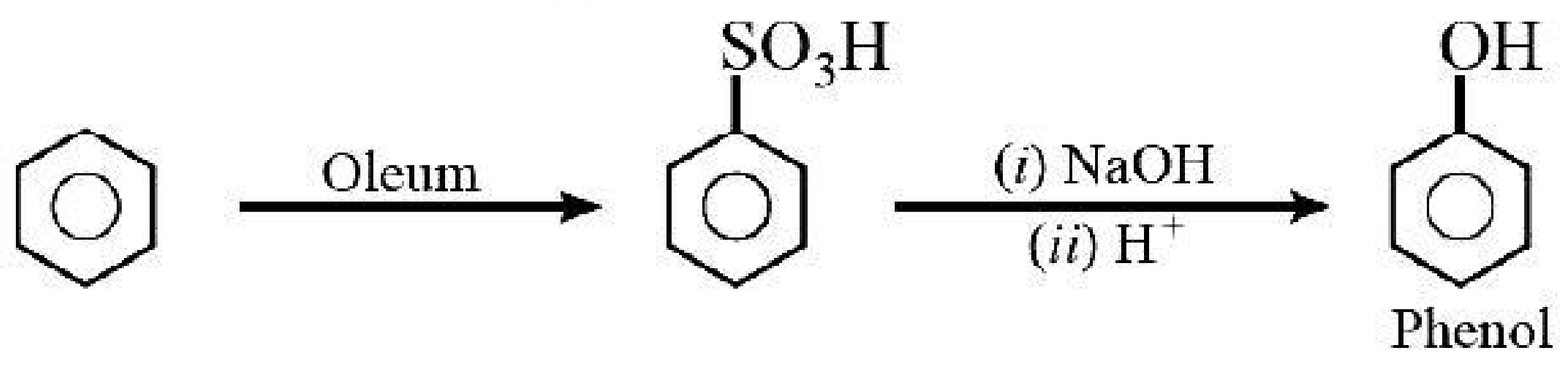


6. Preparation of Phenols:

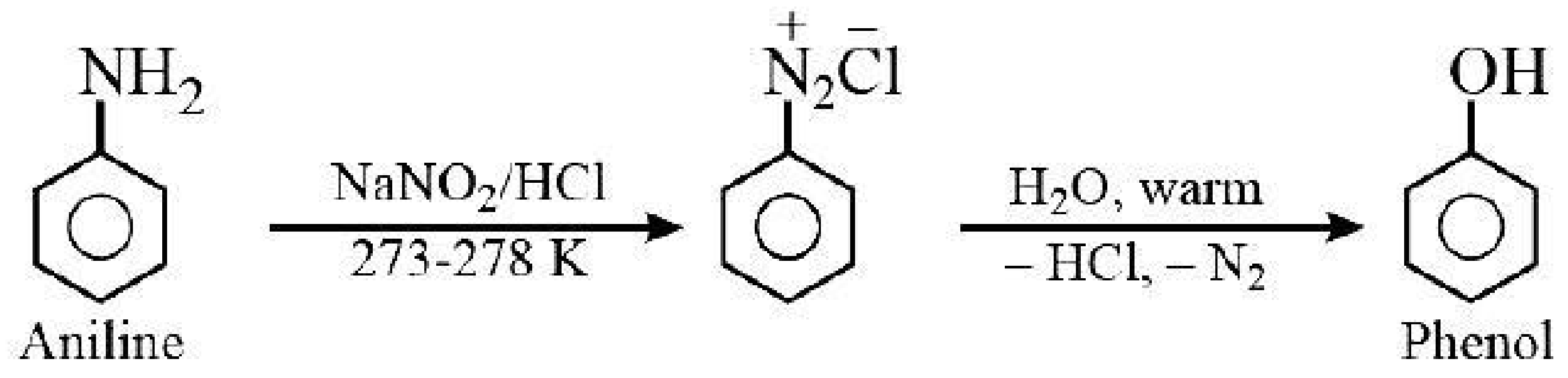
(*i*) From aryl halides



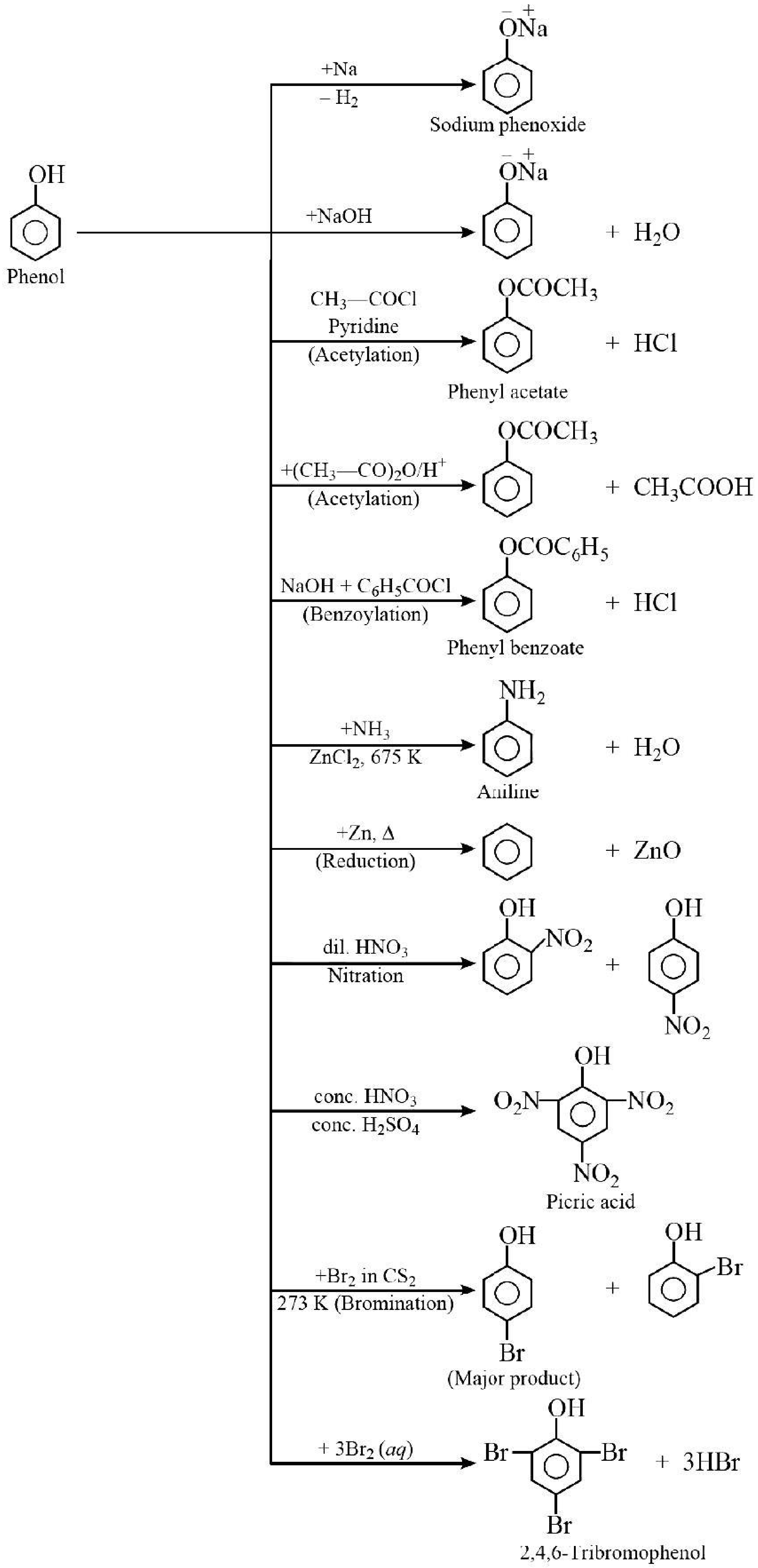
(*ii*) From benzene sulphonic acid



(*iii*) From diazonium salts



7. Reactions of Phenol:

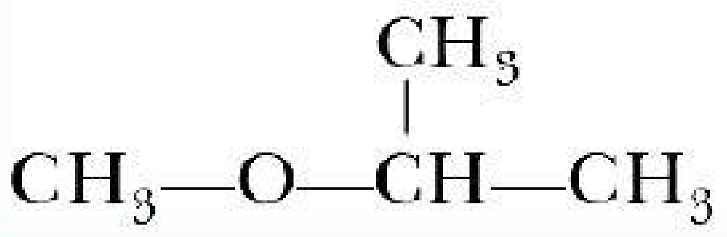
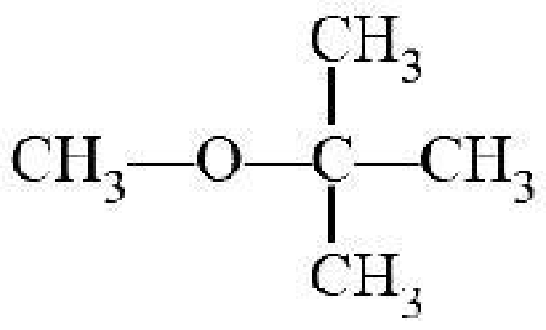
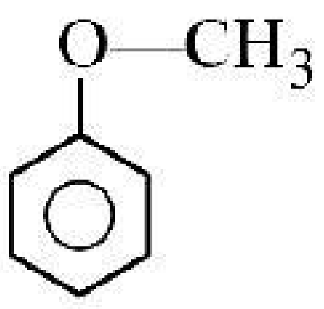
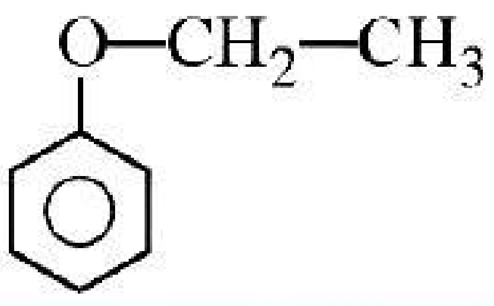
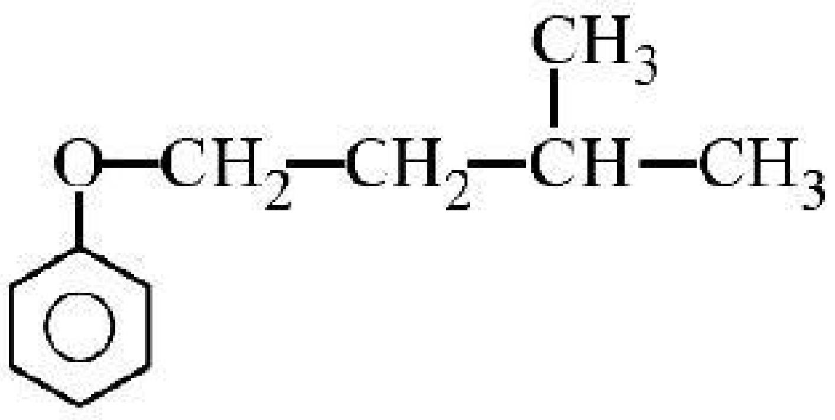


8. **Ethers:** Ethers are the compounds with general formula of $C_nH_{2n+2}O$ (same as monohydric alcohols). These are represented by general structure, R—O—R′.

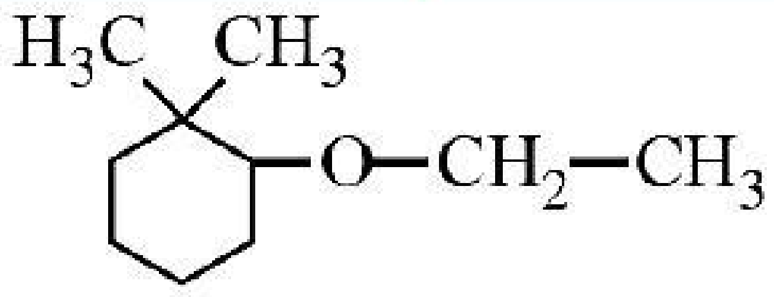
The groups R and R′ in ether may either be same or different. In case these groups are same, the compounds are known as simple ethers or symmetrical ethers. On the other hand, if R and R′ groups are different, the compounds are called mixed ether or unsymmetrical ethers.

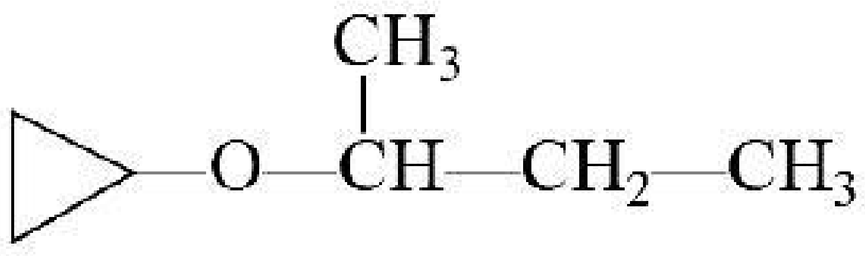
Nomenclature: According to IUPAC system, ethers are named as alkoxyalkanes. The larger alkyl group forms the part of parent chain while smaller alkyl group constitutes the alkoxy group.

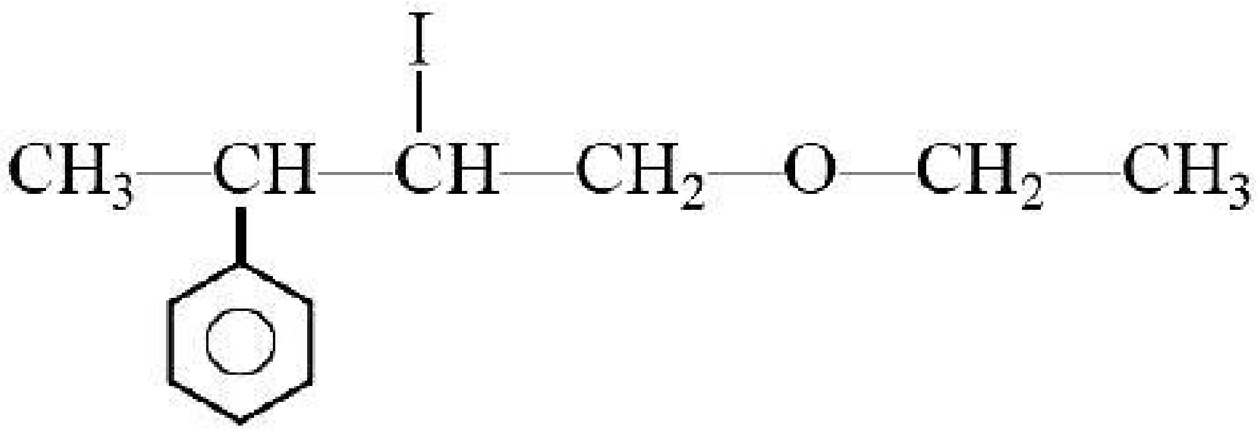
Table 11.1: Common and IUPAC Names of Some Ethers

Common Name	Structural Formula	IUPAC Name
Dimethyl ether	$CH_3—O—CH_3$	Methoxymethane
Diethyl ether	$CH_3—CH_2—O—CH_2—CH_3$	Ethoxyethane
Methyl isopropyl ether	 $CH_3—O—\overset{\overset{\large CH_3}{\vert}}{CH}—CH_3$	2-Methoxypropane
Methyl tert.-butyl ether	 $CH_3—O—\underset{\underset{\large CH_3}{\vert}}{\overset{\overset{\large CH_3}{\vert}}{C}}—CH_3$	2-Methoxy-2-methylpropane
Anisole		Methoxybenzene
Phenetole		Ethoxybenzene
Phenyl isopentyl ether		3-Methyl-butoxybenzene

$CH_3—O—CH_2—CH_2—O—CH_3$
1, 2-Dimethoxyethane


2-Ethoxy-1, 1-dimethylcyclohexane


2-Cyclopropoxybutane


1-Ethoxy -2-iodo-3-phenylbutane

9. **Preparation of Ethers:**

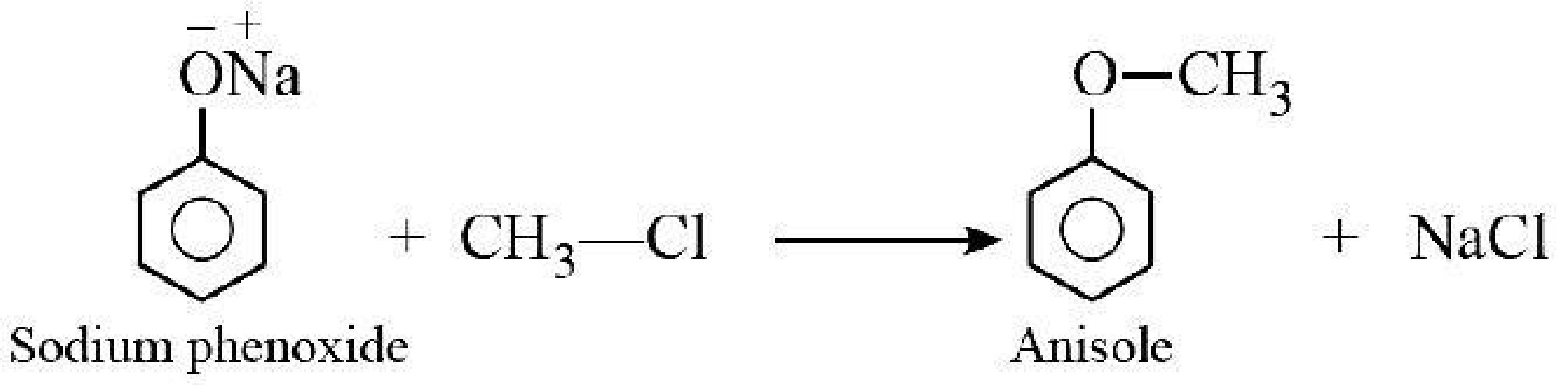
(*a*) **By dehydration of alcohols**

$$\underset{\text{(excess)}}{2CH_3—CH_2—OH} \xrightarrow[\text{413 K}]{\text{conc. } H_2SO_4} \underset{\text{Diethyl ether}}{CH_3—CH_2—O—CH_2—CH_3} + H_2O$$

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

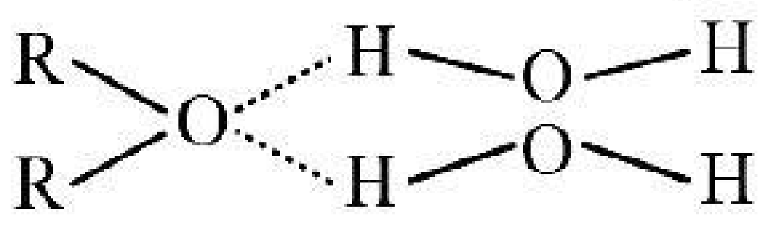
(*b*) Williamson synthesis

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



10. Physical Properties:

1. **Physical state:** The lower homologues of ethers are colourless, pleasant smelling, volatile liquids with a typical 'ether' smell.
2. **Boiling points:** Ethers have much lower boiling points as compared to isomeric alcohols. Unlike alcohols, ether molecules are not associated by hydrogen bonds. The interparticle forces existing in their liquid states are weak dipole–dipole forces.
3. **Solubility:** The solubility of ethers is comparable to those of corresponding alcohols. The solubility of ethers is due to the ability of their molecules to form hydrogen bond with water molecules.



However, solubility of ethers in water decreases from lower members to higher members. This is because of the relative increase in the hydrocarbon portion of the molecule which decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone, etc.

11. Chemical Reactions:

Chemical Reactions: Ethers are relatively inert compounds in spite of the presence of oxygen atom carrying two lone pairs of electrons in their molecules. It is because of this reason that these are used as solvents. They undergo chemical reactions under specific conditions. Some of the reactions of ethers are being described as follows:

(*a*) Cleavage of C—O bond: Carbon oxygen bond in ethers can be cleaved by the use of reagents like halogen acids, sulphuric acid and phosphorus pentachloride, etc.

Cleavage with halogen acid: Ethers can be cleaved by the use of hydroiodic acid or hydrobromic acid to give alkyl halide and alcohol.

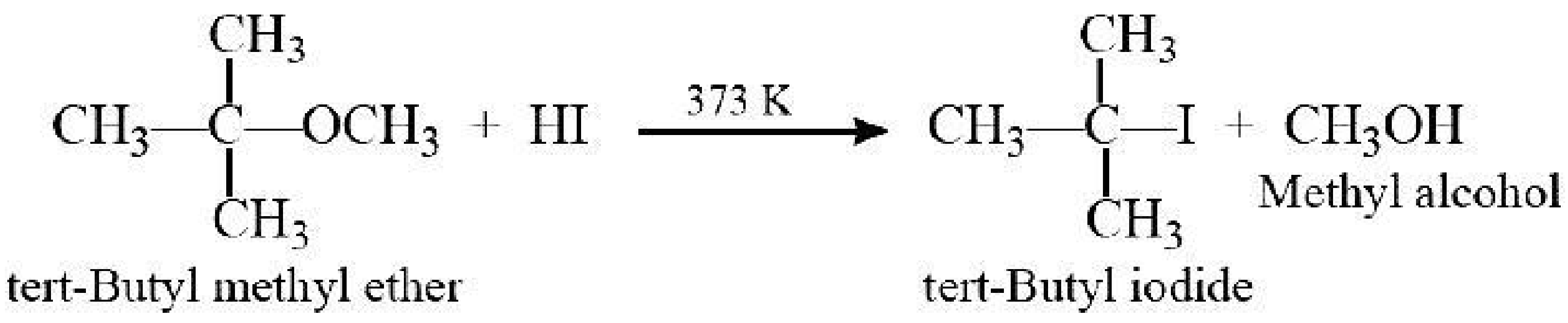
$$\underset{\text{Ether}}{R—O—R} + HX \xrightarrow{373\text{ K}} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX} \quad (X = Br, I)$$

$$C_2H_5OC_2H_5 + HI \xrightarrow{373\text{ K}} C_2H_5OH + C_2H_5I$$

In case excess of HI is used, the alcohol formed reacts further with HI to form alkyl iodide. The overall reaction can be written as

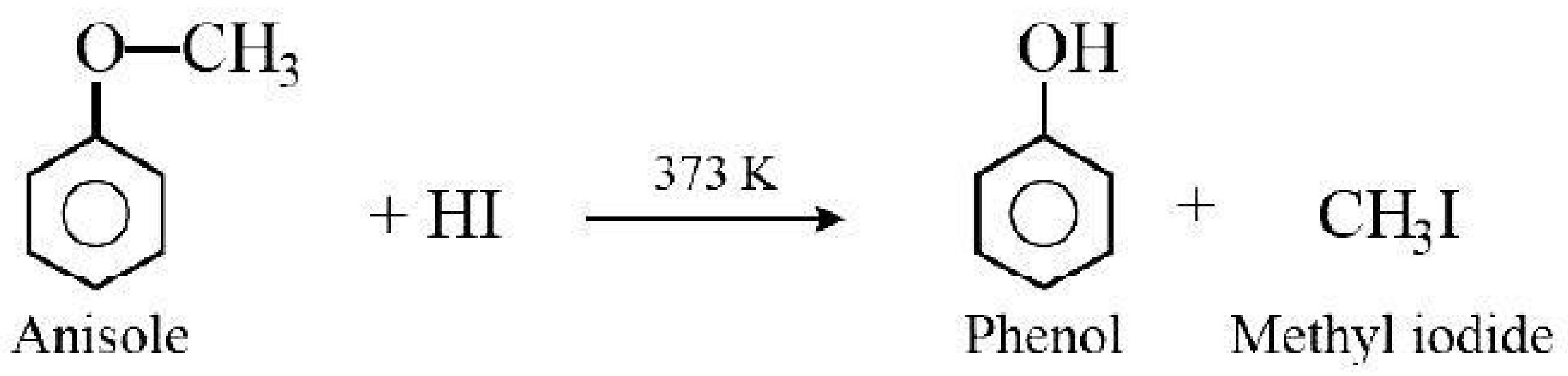
$$C_2H_5OC_2H_5 + \underset{\text{(Excess)}}{2HI} \xrightarrow{373\text{ K}} 2C_2H_5I + H_2O$$

If one group is methyl and other group is tertiary alkyl group, the main product is methyl alcohol and tertiary alkyl halide. It is because the departure of leaving group (CH_3—OH) creates a more stable tertiary carbocation.



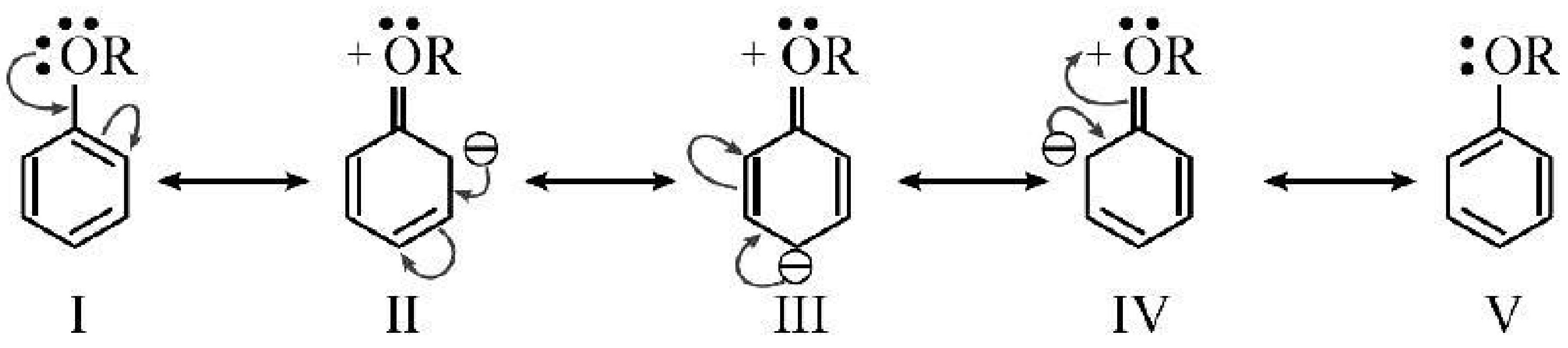
$$\underset{\text{tert-Butyl methyl ether}}{CH_3—\overset{CH_3}{\underset{CH_3}{C}}—OCH_3} + HI \xrightarrow{373\text{ K}} \underset{\text{tert-Butyl iodide}}{CH_3—\overset{CH_3}{\underset{CH_3}{C}}—I} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

In case of anisole, the products formed are phenol and methyl iodide.

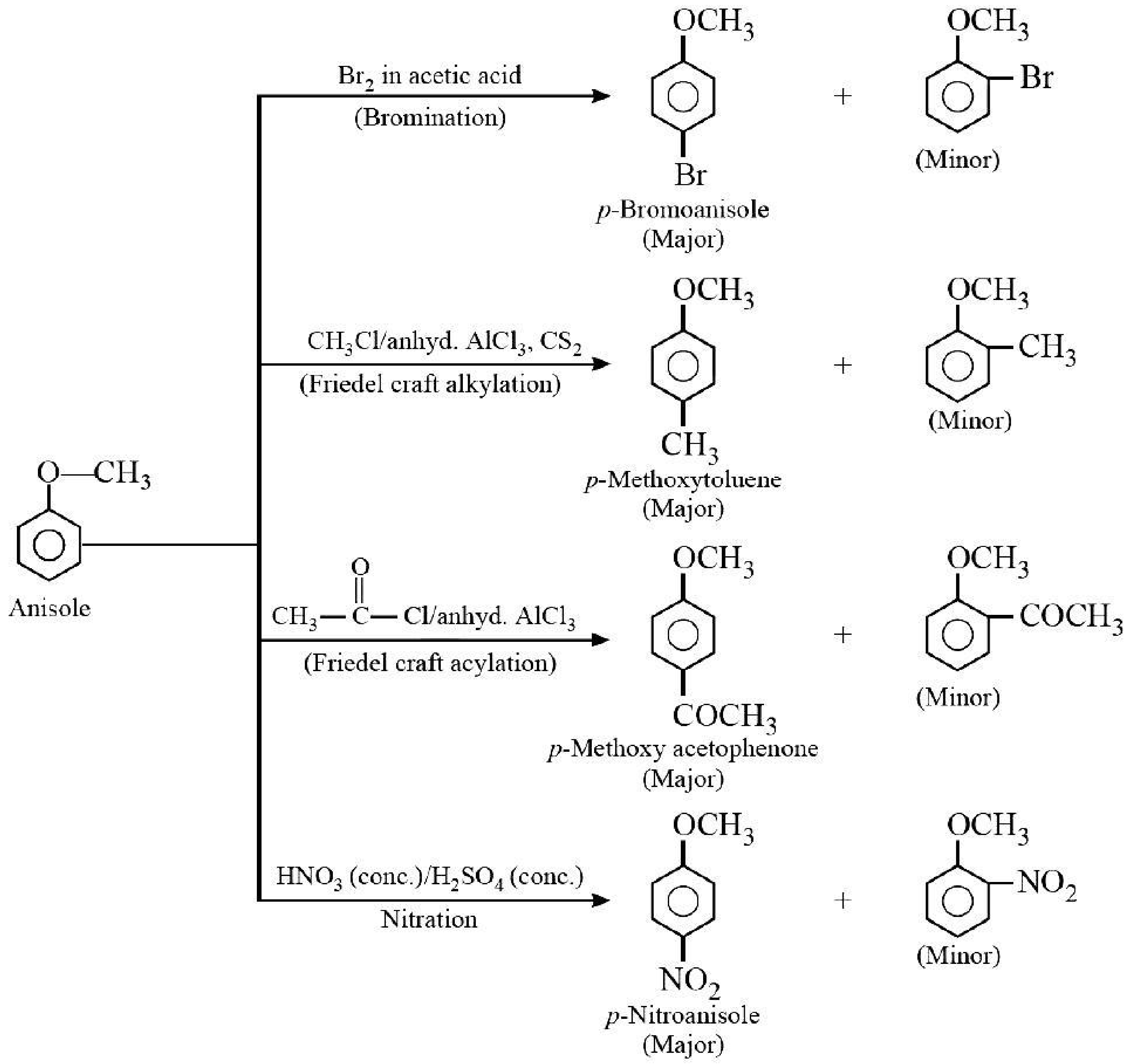


The bond between O—CH_3 is weaker than the bond between O—C_6H_5 because the carbon of phenyl group is sp^2 hybridised and there is a partial double bond character. Therefore, the attack of I^- ion breaks O—CH_3 bond to form CH_3I.

(b) Ring substitution in aromatic ethers: The alkoxy group (—OR) attached to aromatic ring activates the ring towards electrophilic substitution and directs the incoming electrophile to ortho and para positions.

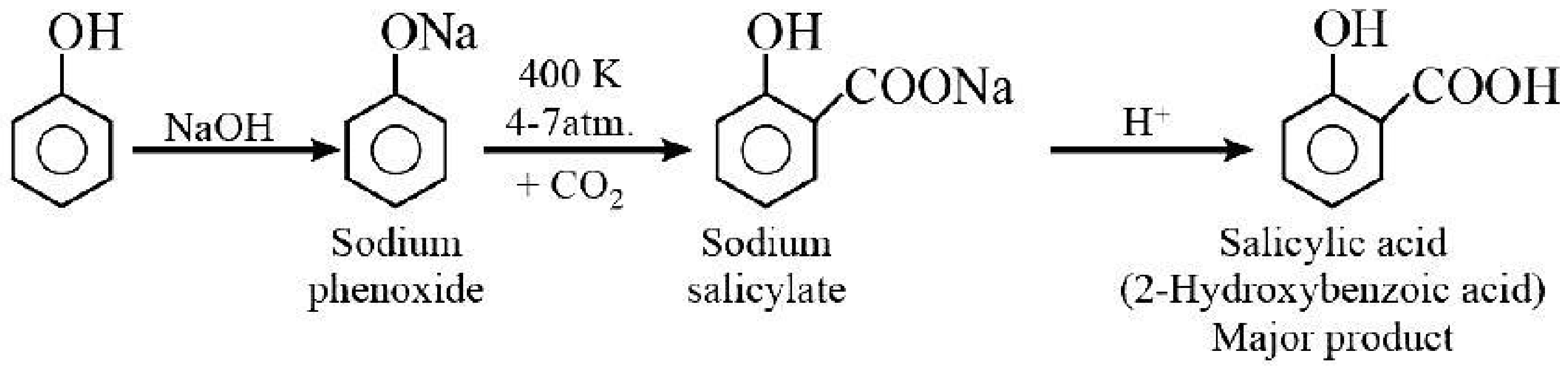


The presence of negative charge at ortho and para positions indicates that electron density is more at these positions. Therefore, electrophile is likely to attack on these positions resulting in the formation of ortho and para substituted products.

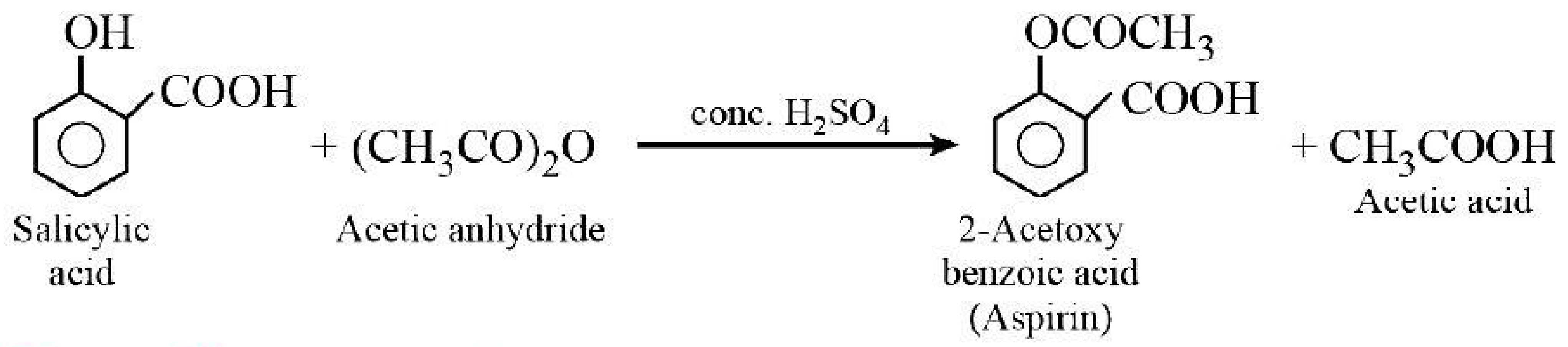


12. Some Important Name Reactions

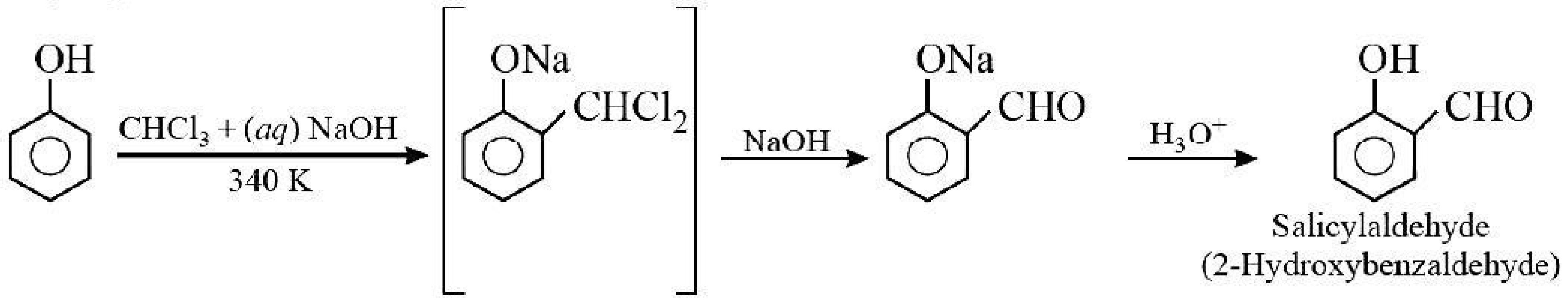
(i) Kolbe's reaction: When sodium phenoxide is heated with CO_2 at 400 K under a pressure of 4 –7 atm, the resulting product on acidification yields salicylic acid.



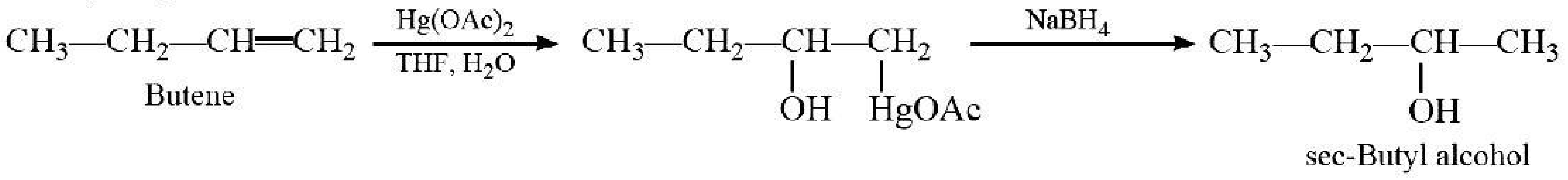
Salicylic acid is the starting material for the manufacture of 2-acetoxybenzoic acid (aspirin).



(*ii*) **Reimer–Tiemann reaction:** Treatment of phenol with chloroform in the presence of aqueous alkali at 340 K followed by hydrolysis of resulting product gives *o*-hydroxybenzaldehyde (salicylaldehyde) as a major product.

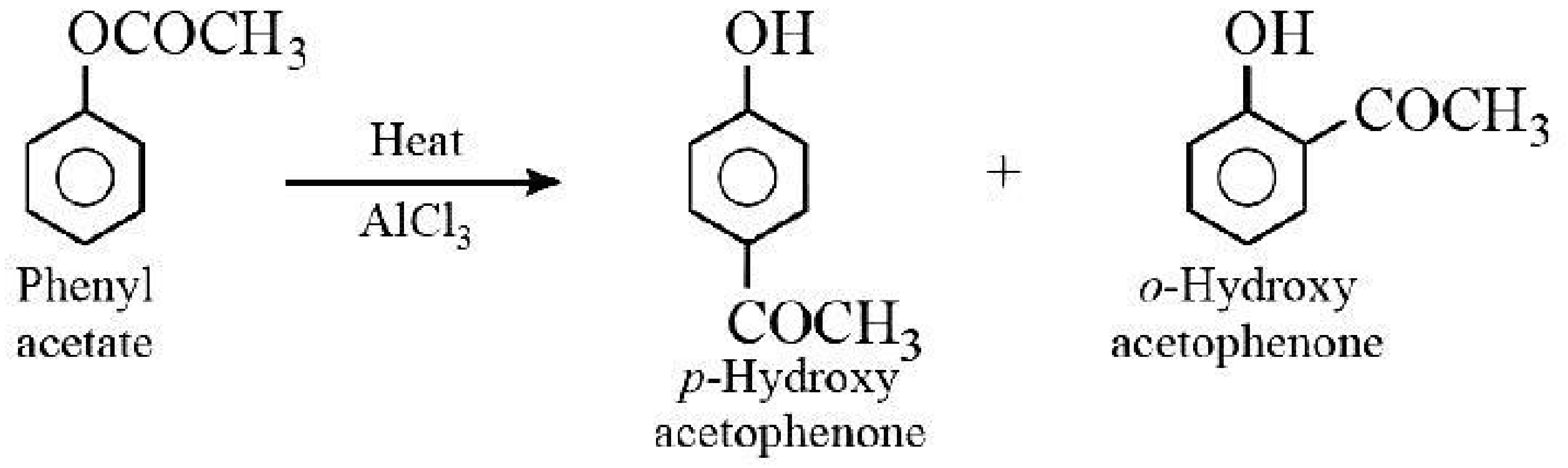


(*iii*) **Oxymercuration and demercuration of alkenes:** Alkenes react with mercuric acetate in a mixture of tetrahydrofuran and water to give hydroxy mercurial compound, involving addition of —OH and —HgOAc to the double bond. This is called oxymercuration. Then $NaBH_4$ reduces —HgOAc and replaces with hydrogen. This is called demercuration.



$$\underset{\text{Butene}}{CH_3{-}CH_2{-}CH{=}CH_2} \xrightarrow[\text{THF, }H_2O]{Hg(OAc)_2} CH_3{-}CH_2{-}\underset{OH}{\underset{|}{CH}}{-}\underset{HgOAc}{\underset{|}{CH_2}} \xrightarrow{NaBH_4} \underset{\text{sec-Butyl alcohol}}{CH_3{-}CH_2{-}\underset{OH}{\underset{|}{CH}}{-}CH_3}$$

(*iv*) **Fries rearrangement:** Phenyl esters on heating with anhydrous $AlCl_3$ in the presence of CS_2 as solvent undergo rearrangement to give ortho and para hydroxyketones. This rearrangement is known as Fries rearrangement.



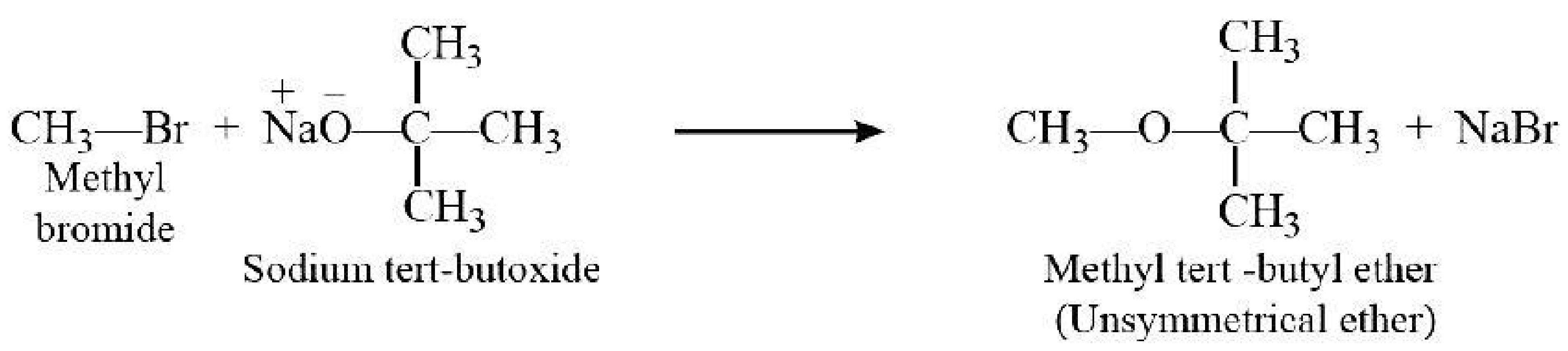
The reaction involves migration of acyl group from phenolic oxygen to the ortho or para position of the aromatic ring.

(*v*) **Williamson synthesis:** It consists of reacting an alkyl halide with sodium alkoxide or sodium phenoxide to form ether.

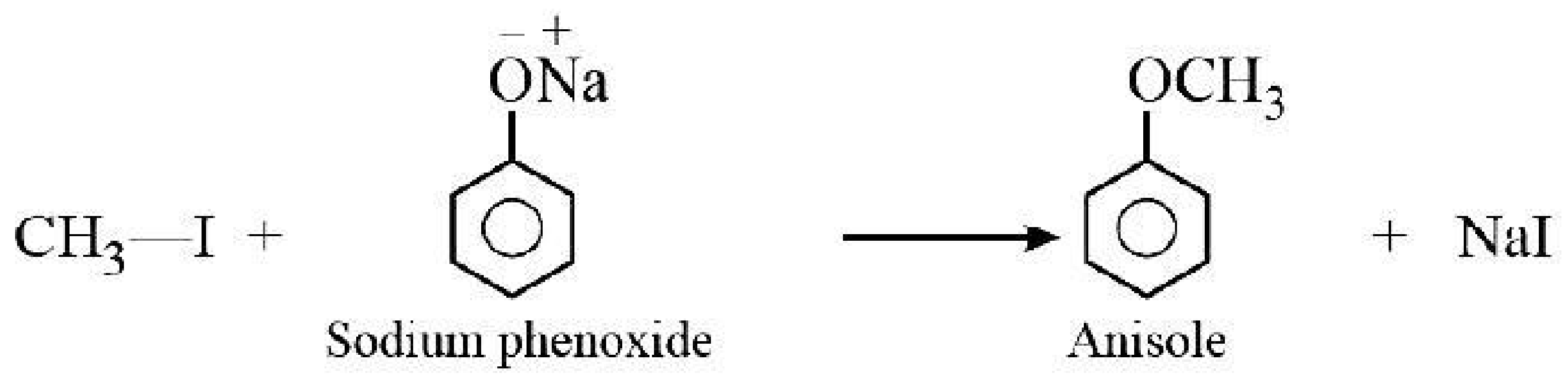
$$\underset{\text{Alkyl halide}}{R{-}X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}{-}\overset{-}{O}{-}R'} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R'} + NaX$$

It is a convenient method for the preparation of symmetrical as well as unsymmetrical ethers.

$$\underset{\text{Ethyl iodide}}{CH_3{-}CH_2{-}I} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}{-}\overset{-}{O}{-}CH_2{-}CH_3} \longrightarrow \underset{\text{Diethyl ether (Symmetrical ether)}}{CH_3{-}CH_2{-}O{-}CH_2{-}CH_3} + NaI$$



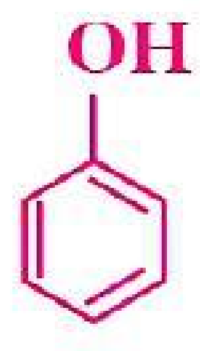
$$\underset{\text{Methyl bromide}}{CH_3{-}Br} + \underset{\text{Sodium tert-butoxide}}{\overset{+}{Na}\overset{-}{O}{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3} \longrightarrow \underset{\text{Methyl tert -butyl ether (Unsymmetrical ether)}}{CH_3{-}O{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_3} + NaBr$$



MULTIPLE CHOICE QUESTIONS

Choose and write the correct option in the following questions.

1. Which of the following compounds is aromatic alcohol? *[NCERT Exemplar]*


(A)


(B)


(C)


(D)

(*a*) A, B, C, D (*b*) A, D (*c*) B, C (*d*) A

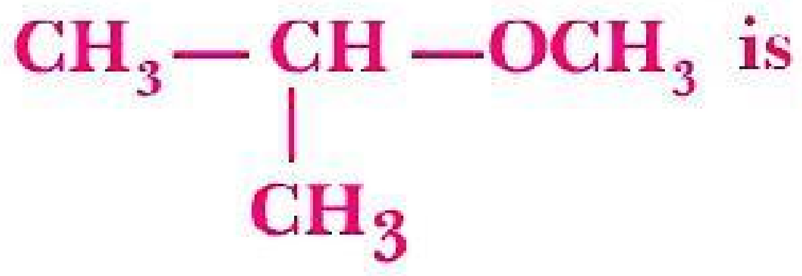
2. How many alcohols with molecular formula $C_4H_{10}O$ are chiral in nature? *[NCERT Exemplar]*

(*a*) 1 (*b*) 2 (*c*) 3 (*d*) 4

3. IUPAC name of *m*-cresol is ______________. *[NCERT Exemplar]*

(*a*) 3-methylphenol (*b*) 3-chlorophenol (*c*) 3-methoxyphenol (*d*) benzene-1, 3-diol

4. IUPAC name of the compound


$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-OCH_3$

is ______________. *[NCERT Exemplar]*

(*a*) 1-methoxy-1-methylethane (*b*) 2-methoxy-2-methylethane

(*c*) 2-methoxypropane (*d*) isopropylmethyl ether

5. The C—O bond length in phenol is less than that in methanol due to

(*a*) partial double bond character in aromatic ring

(*b*) sp^2 hybridised carbon

(*c*) sp^3 hybridised carbon

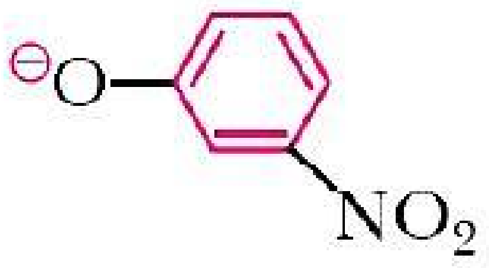
(*d*) both (*a*) and (*b*)

6. The order of reactivity of the alkenes, (*i*) $(CH_3)_2C{=}CH_2$, (*ii*) $CH_3CH{=}CH_2$, (*iii*) $CH_2{=}CH_2$, when subjected to acid catalysed hydration is:

(*a*) (*i*) > (*iii*) > (*ii*) (*b*) (*i*) > (*ii*) > (*iii*) (*c*) (*ii*) > (*i*) > (*iii*) (*d*) (*iii*) > (*ii*) > (*i*)

7. Which of the following species can act as the strongest base? *[NCERT Exemplar]*

(*a*) $^{\ominus}OH$ (*b*) $^{\ominus}OR$ (*c*) $^{\ominus}OC_6H_5$ (*d*)



8. Phenol is less acidic than ______________. *[NCERT Exemplar]*

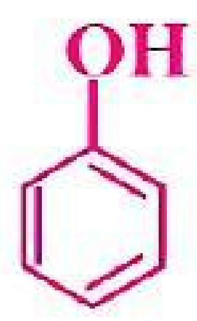
(*a*) ethanol (*b*) *o*-nitrophenol (*c*) *o*-methylphenol (*d*) *o*-methoxyphenol

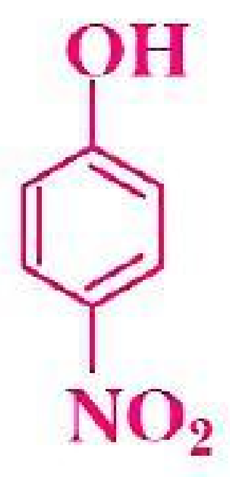
9. Which is the correct order of acid strength of the following?

(*a*) $C_6H_5OH > H_2O > ROH > HC{\equiv}CH$ (*b*) $C_6H_5OH > ROH > H_2O > HC{\equiv}CH$

(*c*) $C_6H_5OH > HC{\equiv}CH > H_2O > ROH$ (*d*) $C_6H_5OH > H_2O > HC{\equiv}CH > ROH$

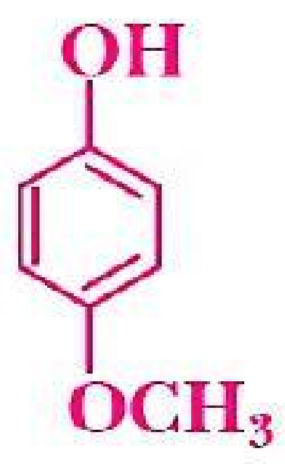
10. Mark the correct order of decreasing acid strength of the following compounds. *[NCERT Exemplar]*


(*i*)


(*ii*)


(*iii*)


(*iv*)


(*v*)

(*a*) (*v*) > (*iv*) > (*ii*) > (*i*) > (*iii*) (*b*) (*ii*) > (*iv*) > (*i*) > (*iii*) > (*v*)

(*c*) (*iv*) > (*v*) > (*iii*) > (*ii*) > (*i*) (*d*) (*v*) > (*iv*) > (*iii*) > (*ii*) > (*i*)

11. In the reaction given below, X is:

$$\text{Neopentyl alcohol} \xrightarrow{H_2SO_4} X$$

(*a*) 2-methylpent-2-ene (*b*) 2-methylpentane (*c*) 2-methylbut-2-ene (*d*) neopentane

12. Tertiary alcohols on reaction with $KMnO_4$ at elevated temperature form

(*a*) aldehyde

(*b*) ketone

(*c*) mixture of carboxylic acids containing lesser number of carbon atoms

(*d*) mixture of carboxylic acids containing more number of carbon atoms

13. What is the correct order of reactivity of alcohols in the following reaction?

$$R—OH + HCl \xrightarrow{ZnCl_2} R—Cl + H_2O$$ *[NCERT Exemplar]*

(*a*) 1° > 2° > 3° (*b*) 1° < 2° > 3° (*c*) 3° > 2° > 1° (*d*) 3° > 1° > 2°

14. The compound that reacts fastest with Lucas reagent at room temperature is

(*a*) butan-1-ol (*b*) butan-2-ol

(*c*) 2 methylpropan-1-ol (*d*) 2-methylpropan-2-ol

15. CH_3CH_2OH can be converted into CH_3CHO by ______________. *[NCERT Exemplar]*

(*a*) catalytic hydrogenation (*b*) treatment with $LiAlH_4$

(*c*) treatment with pyridinium chlorochromate (*d*) treatment with $KMnO_4$

16. An alcohol on oxidation is found to give CH_3COOH and CH_3CH_2COOH. The structure of the alcohol is:

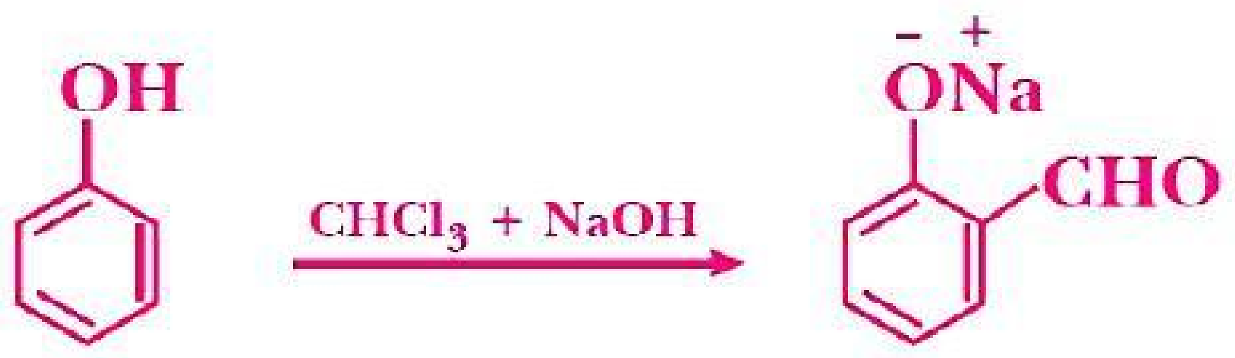
(*a*) $CH_3CH_2CH_2OH$ (*b*) $(CH_3)_2C(OH)CH_2—CH_3$

(*c*) $CH_3(CH_2)_3CH_2OH$ (*d*) $CH_3CH(OH)CH_2CH_2CH_3$

17. Which of the following compounds will react with sodium hydroxide solution in water?
[NCERT Exemplar]

(*a*) C_6H_5OH (*b*) $C_6H_5CH_2OH$ (*c*) $(CH_3)_3$ COH (*d*) C_2H_5OH

18.



The electrophile involved in the above reaction is:

(*a*) ^{+}CHO (*b*) $^{+}CHCl_2$ (*c*) $^{-}CCl_3$ (*d*) $:CCl_2$

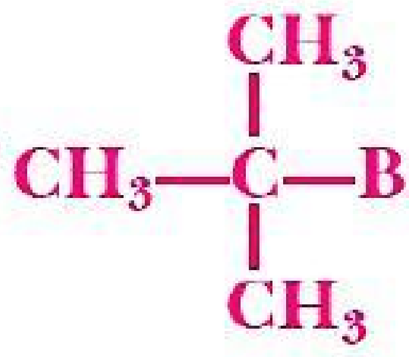
19. Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields. *[NCERT Exemplar]*

(*a*) *o*-Cresol (*b*) *m*-Cresol

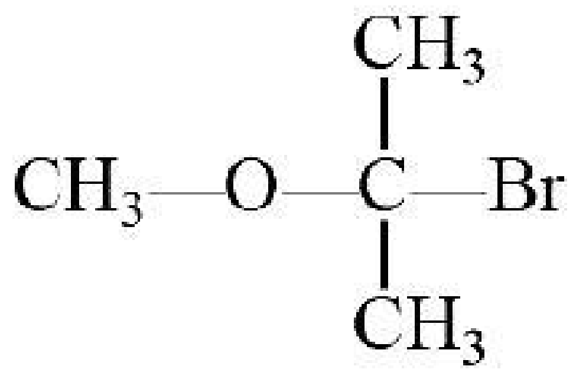
(*c*) 2, 4-Dihydroxytoluene (*d*) Benzyl alcohol

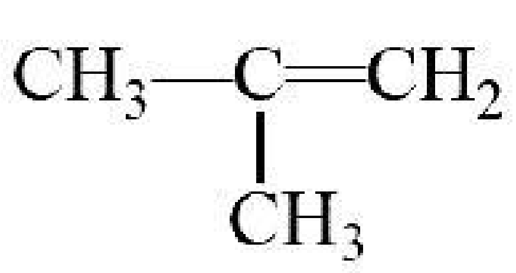
20. Which of the following compounds is oxidised to methyl ethyl ketone?

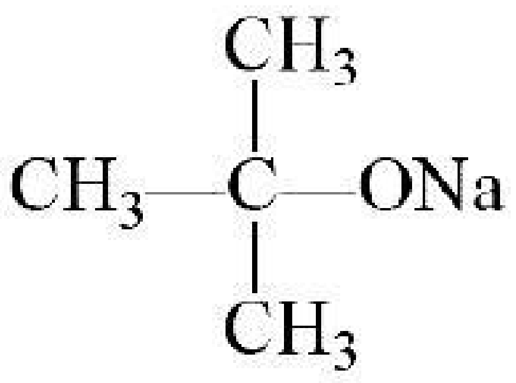
(*a*) 2-Propanol (*b*) 1-Butanol (*c*) 2-Butanol (*d*) *tert*. Butyl alcohol

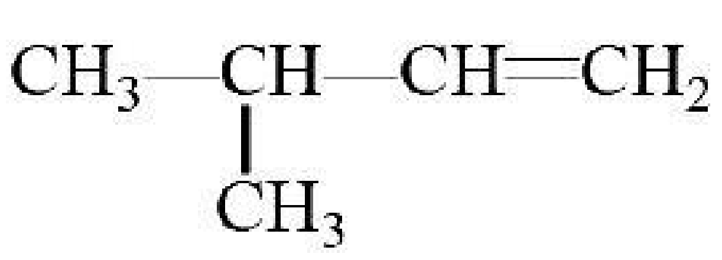


21. The reaction of $CH_3—\overset{CH_3}{\underset{CH_3}{C}}—Br$ with $NaOCH_3$ forms the product,

(*a*)

$CH_3—O—\overset{CH_3}{\underset{CH_3}{C}}—Br$

(*b*)

$CH_3—\underset{CH_3}{C}{=}CH_2$

(*c*)

$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—ONa$

(*d*)

$CH_3—\underset{CH_3}{CH}—CH{=}CH_2$

22. Treatment of phenol with Br_2/H_2O yields

(*a*) *o*–bromophenol (*b*) *m*–bromophenol

(*c*) 2,4,6–tribromophenol (*d*) *p*–bromophenol

23. Picric acid is

(*a*) trinitrotoluene (*b*) *o*-nitrophenol

(*c*) 2,4,6–trinitrophenol (*d*) phenol

24. Phenol on distillation with Zn dust produces

(*a*) zinc phenoxide (*b*) benzene (*c*) *o*–chlorophenol (*d*) benzylalcohol

25. Which of the following is a ring activating group?

(*a*) $—NO_2$ (*b*) —COOH (*c*) —CHO (*d*) —OH

26. The reaction between phenol, chloroform and aq. alkali solution is called as

(*a*) Claisen reaction (*b*) Wurtz reaction

(*c*) Reimer-Tiemann reaction (*d*) Cannizzaro's reaction

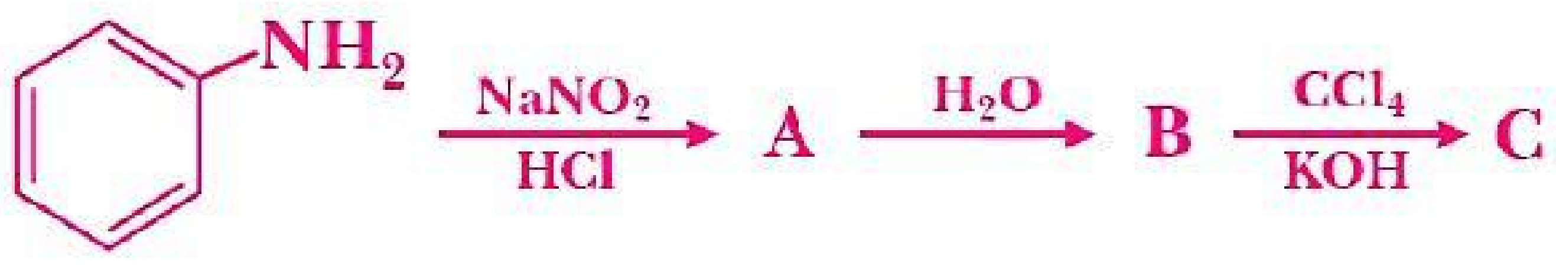
27. ____________ is called as carbolic acid.

(*a*) $C_6H_5—COOH$ (*b*) $C_6H_5—CHO$ (*c*) $C_6H_5—OH$ (*d*) H_2CO_3

28. Benzyl alcohol and phenol can be distinguished by

(*a*) Lucas reagent (*b*) $FeCl_3$ (*c*) PCl_5 (*d*) Na–metal

29. Identify the product 'C'.



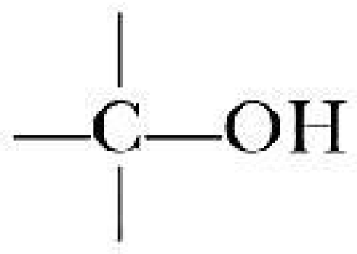
(*a*) Salicylaldehyde (*b*) Salicylic acid (*c*) Phenol (*d*) Benzoic acid

30. Which one is the general formula of monohydric alcohol?

(*a*) $C_nH_{2n}OH$ (*b*) $C_{n+1}H_{2n}OH$ (*c*) $C_nH_{2n+2}OH$ (*d*) $C_nH_{2n+1}OH$

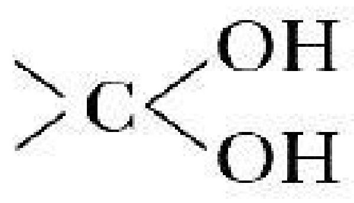
31. Which of the following compounds is/are primary alcohol?

(*a*) $>CHOH$ (*b*)



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

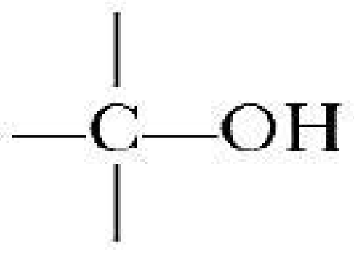
(*c*) $—CH_2OH$ (*d*)



$>C<\begin{matrix}OH\\OH\end{matrix}$

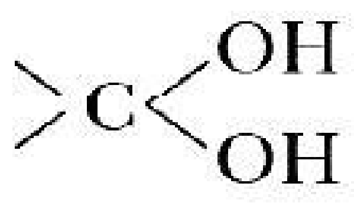
32. The characteristic group of secondary alcohol is

(*a*) $—CH_2OH$ (*b*) $>CHOH$ (*c*)



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

(*d*)



$>C<\begin{matrix}OH\\OH\end{matrix}$

33. Ethane 1, 2-diol is an example of

(*a*) monohydric alcohol (*b*) trihydric alcohol (*c*) secondary alcohol (*d*) dihydric alcohol

34. Butan-2-ol is a

(*a*) a primary alcohol (*b*) a secondary alcohol (*c*) a tertiary alcohol (*d*) an aldehyde

35. Which one is primary alcohol?

(*a*) Butan-2-ol (*b*) Butan-1-ol

(*c*) Propan-2-ol (*d*) 2, 3-Dimethyl hexan-4-ol

36. Alcohols are soluble in water because

(*a*) alcohol forms ionic bond with water.

(*b*) alcohol forms hydrogen bond with water.

(*c*) alcohol forms covalent bond with water.

(*d*) alcohol forms interstitial compound with water.

37. When a mixture of methyl alcohol and air is passed through a heated tube containing iron powder and molybdenum oxide, which one of these is formed?

(*a*) CO (*b*) CO_2 (*c*) HCHO (*d*) CH_3CHO

38. Glycerol on warming with a small amount of HI, gets converted into

(*a*) $CH_3CH = CH_2$ (*b*) CH_3CHICH_3 (*c*) $CH_2I—CHICH_2I$ (*d*) $CH_2 = CHCH_2I$

39. Which of these when passed over heated Cu at 573 K forms an alkene?

(*a*) An alkane (*b*) An alkyne (*c*) Secondary alcohol (*d*) Tertiary alcohol

40. Phenol on heating with chloroform and conc. KOH gives

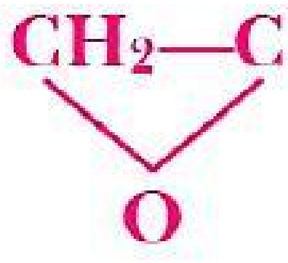
(*a*) salicylic acid (*b*) salicylaldehyde (*c*) benzaldehyde (*d*) chlorobenzene

41. Ethanol on heating with conc. H_2SO_4 at 445 K gives

(*a*) $C_2H_5HSO_4$ (*b*) $C_2H_5OC_2H_5$ (*c*) $CH_2 = CH_2$ (*d*) $(C_2H_5)_2SO_4$

42. Which of the following reagents cannot be used to distinguish phenol from ethanol?

(*a*) $FeCl_3$ (*b*) NaOH (*c*) Na (*d*) Br_2/H_2O

43. The reaction of  with RMgX leads to the formation of

(*a*) RCHOHR (*b*) $RCHOHCH_3$ (*c*) R_2CHCH_2OH (*d*) RCH_2CH_2OH

44. Which one of the following compounds will be most readily attacked by an electrophile?

(*a*) Chlorobenzene (*b*) Benzene (*c*) Phenol (*d*) Toluene

45. Aspirin is an acetylation product of

(*a*) *p*-Dihydroxybenzene (*b*) *o*-Hydroxybenzoic acid

(*c*) *o*-Dihydroxybenzoic acid (*d*) *m*-Hydroxybenzoic acid

46. Ethers have a net dipole moment because

(*a*) C—C bonds are polar in ether. (*b*) C—C bonds are non-polar in ether.

(*c*) C—O bonds are polar in ether. (*d*) C—O bonds are non-polar in ether.

47. The ionization constant of phenol is higher than ethanol because

(*a*) phenoxide ion is stronger base than ethoxide ion.

(*b*) phenoxide ion is stabilized through delocalization.

(*c*) phenoxide ion is less stable than ethoxide ion.

(*d*) phenoxide ion is bulkier than ethoxide ion.

48. The most suitable method of separation of a mixture of ortho and para nitrophenols mixed in 1 : 1 ratio is

(*a*) steam distillation (*b*) crystallization (*c*) vapourization (*d*) colour spectrum

49. The compound obtained by the reaction of ethene with diborane followed by hydrolysis by alkaline hydrogen peroxide is

(*a*) ethanol (*b*) propanol (*c*) ethanal (*d*) triethyl boride

50. Which of the following is most acidic?

(*a*) Phenol (*b*) Benzyl alcohol (*c*) *o*-chlorophenol (*d*) cyclohexanol

51. Which of the following is most suitable method for removing traces of water from ethanol?

(*a*) Heating with Na metal. (*b*) Passing dry HCl gas through it.

(*c*) By distilling. (*d*) Reacting with Mg.

52. Which of the following will not be soluble in sodium bicarbonate?

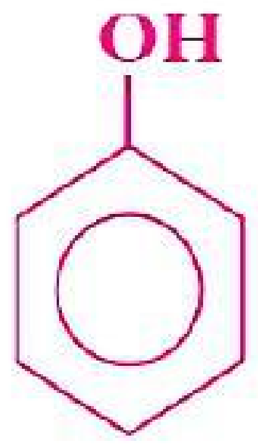
(*a*) 2, 4, 6-trinitrophenol (*b*) Benzoic acid

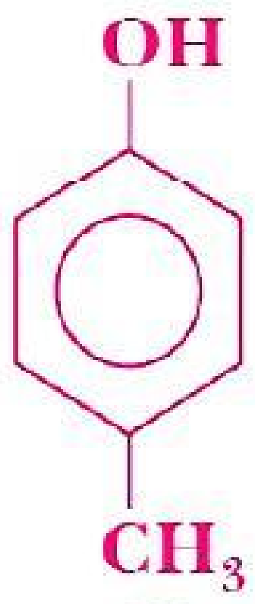
(*c*) o-Nitrophenol (*d*) Benzene sulphonic acid

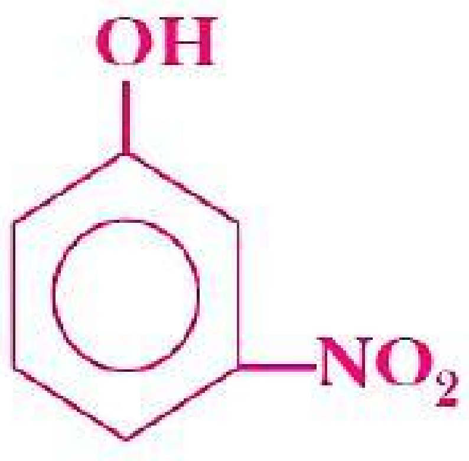
53. An organic compound (X) on treatment with acidified $K_2Cr_2O_7$ gives a compound (Y) which reacts with I_2 and sodium carbonate to form triiodomethane. The compound (X) is

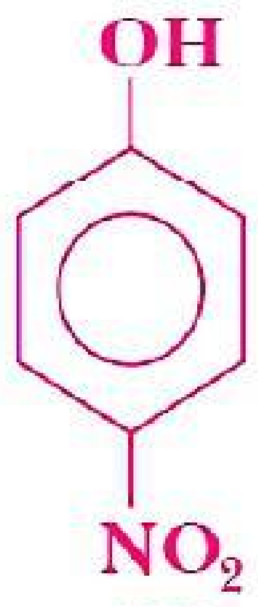
(*a*) CH_3OH (*b*) CH_3COCH_3 (*c*) CH_3CHO (*d*) $CH_3CH(OH)CH_3$

54. In the following compound


(I)


(II)


(III)


(IV)

The order of acidity is

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

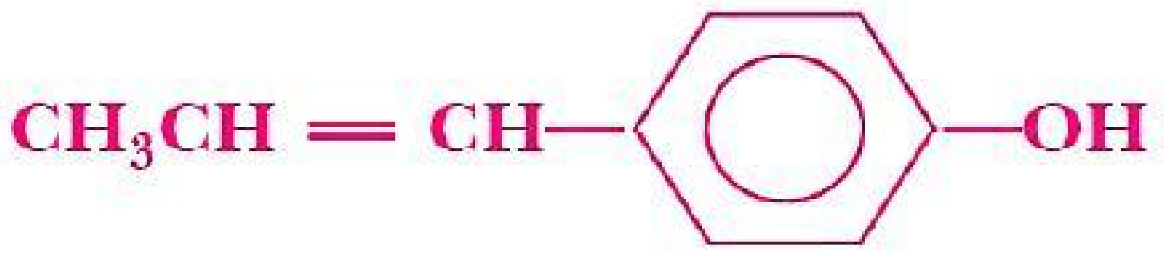
55. Electrophilic substitution in phenol generally occurs at

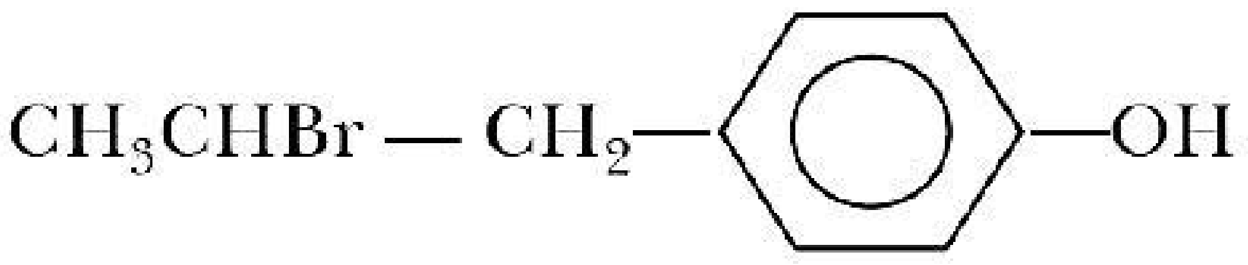
(*a*) para position (*b*) *o* and *p*-positions (*c*) *m*-position (*d*) ortho position

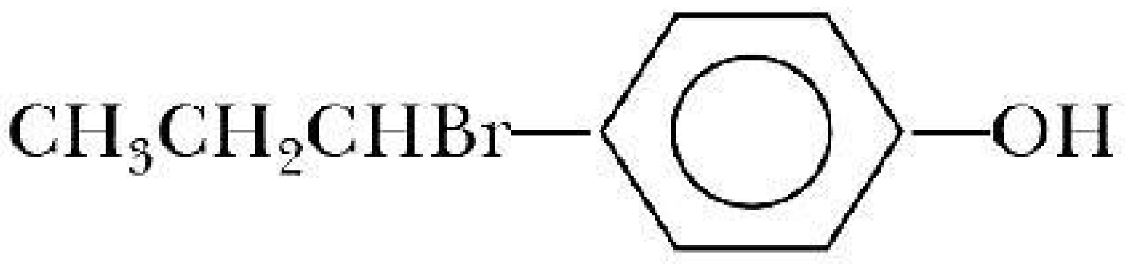
56. Which of the following will give yellow precipitate with I_2 and NaOH?

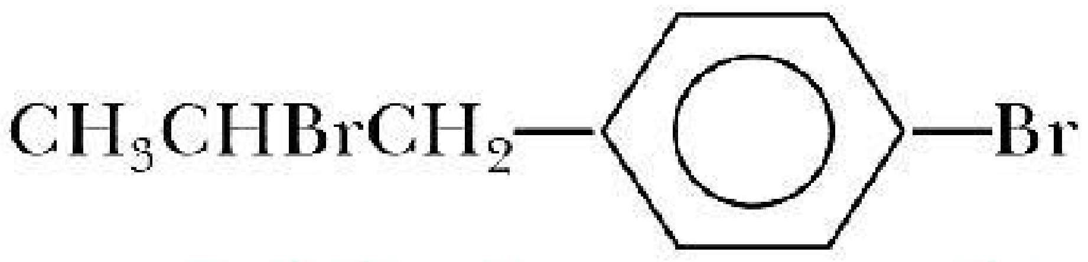
(*a*) $CH_3CH_2COCH_2CH_3$ (*b*) $CH_3COOCOCH_3$

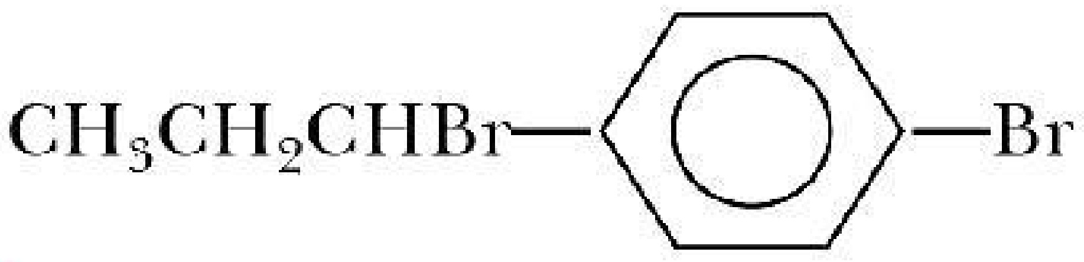
(*c*) CH_3CONH_2 (*d*) $CH_3CH(OH)CH_2CH_3$

57. The reaction of  **with HBr gives**

(*a*) 

(*b*) 

(*c*) 

(*d*) 

58. Among the following compounds, strongest acid is

(*a*) HC ≡ CH (*b*) C_6H_6 (*c*) C_2H_6 (*d*) CH_3OH

59. Diethyl ether on heating with HI gives two moles of

(*a*) ethanol (*b*) iodoform (*c*) ethyl iodide (*d*) methyl iodide

60. Diethyl ether and ethanol are isomeric but ether boils at a much lower temperature because

(*a*) density of ether is less than that of alcohol. (*b*) alcohol mixes with water but ether does not.

(*c*) there is lack of hydrogen bonding in ether. (*d*) there are two methyl groups in ether.

61. Williamson's synthesis is used to prepare

(*a*) alcohols (*b*) ethers (*c*) aldehydes (*d*) amines

62. Preparation of ethers by reacting sodium alkoxide with alkyl halide is called

(*a*) Kolbe's synthesis (*b*) Willamson's synthesis

(*c*) Wurtz reaction (*d*) Cannizzaro's reaction

63. Formation of diethyl ether from ethanol in presence of H_2SO_4 is based on

(*a*) dehydrogenation reaction (*b*) hydrogenation reaction

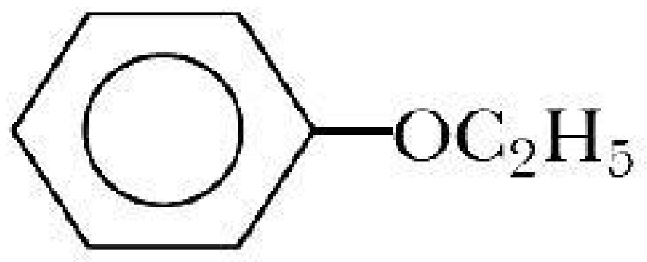
(*c*) dehydration reaction (*d*) heterolytic fission reaction

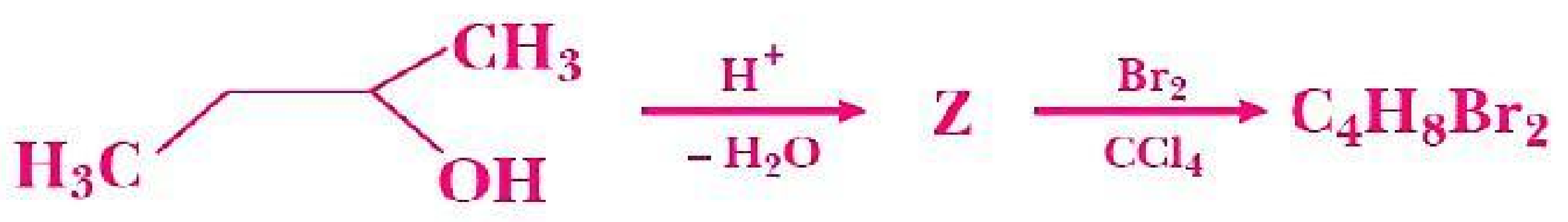
64. An example of a compound having functional group(—O—) is

(*a*) acetone (*b*) acetic acid (*c*) methyl alcohol (*d*) diethyl ether

65. 

A in the equation is :

(*a*)  (*b*) $C_6H_5O—C_6H_5$ (*c*) $C_2H_5—O—C_2H_5$ (*d*) C_6H_5I

66. 

The number of structures of Z possible here is

(*a*) 2 (*b*) 3 (*c*) 5 (*d*) 6

67. Identify the correct order of boiling points of the following compounds?

$CH_3CH_2CH_2CH_2OH$	$CH_3CH_2CH_2CHO$	$CH_3CH_2CH_2COOH$
1	2	3

(*a*) 1 > 2 > 3 (*b*) 3 > 1 > 2 (*c*) 1 > 3 > 2 (*d*) 3 > 2 > 1

68. Propan-1-ol and propan-2-ol can be best distinguished by:

(*a*) Oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution.

(*b*) Oxidation with acidic dichromate followed by reaction with Fehling solution.

(*c*) Oxidation by heating with Cu followed by reaction with Fehling solution.

(*d*) Oxidation with concentrated H_2SO_4 followed by reaction with Fehling solution.

69. The IUPAC name of $C_6H_5—O—C_2H_5$ is

(*a*) ethoxy benzene (*b*) 1-phenyl ethane (*c*) 1-phenoxy ethane (*d*) 2-ethoxy butane

70. Primary, secondary and tertiary alcohols is distinguished by

(*a*) Oxidation method (*b*) Lucas reagent method

(*c*) Primary alcohol and Acid (*d*) Carboxylic acid

71. Which of the following compounds is optically active?

(*a*) butan-1-ol (*b*) butan-2-ol (*c*) propan-1-ol (*d*) propan-2-ol

72. Lucas test is used to distinguish

(*a*) Alcohols (*b*) Alkyl halide (*c*) Amines (*d*) Carbonyl compound

73. A 1% solution of Phenol is a/an

(*a*) antiseptic (*b*) disinfectant (*c*) anti malarial drug (*d*) anti-histamine

74. Acid catalysed hydration of alkene is an example of

(*a*) free radical substitution (*b*) nucleophilic substitution

(*c*) nucleophilic addition (*d*) electrophilic addition

75. The most suitable reagent for the conversion of primary alcohol to aldehyde is

(*a*) PCC (*b*) $K_2Cr_2O_7$ (*c*) $KMnO_4$ (*d*) CrO_3

76. Strongest acid among the following is

(*a*) o-methoxyphenol (*b*) *p*-methoxyphenol (*c*) *m*-methoxyphenol (*d*) phenol

77. Phenol when first treated with concentrated sulphuric acid and then with concentrated nitric acid, gives

(*a*) nitrobenzene (*b*) 2,4,6-trinitrophenol (*c*) *o*-nitrophenol (*d*) *p*-nitrophenol

78. Which of the following ethers is not cleaved by HI

(*a*) Dicyclohexyl ether (*b*) Phenetol (*c*) Di-tert-butyl ether (*d*) Diphenyl ether

79. The reaction can be classified as

(*a*) Dehydration reaction (*b*) Williamson alcohol synthesis reaction

(*c*) Williamson ether synthesis reaction (*d*) Alcohol formation reaction

80. Ethanol is converted into ethoxy ethane

(*a*) by heating excess of ethanol with conc. H_2SO_4 at 140°C.

(*b*) by heating Ethanol with excess of conc. H_2SO_4 at 443 K.

(*c*) by treating with conc. H_2SO_4 at room temperature.

(*d*) by treating with conc. H_2SO_4 at 273 K.

81. Isopropyl methyl ether when treated with cold hydrogen iodide gives

(*a*) isopropyl iodide and methyl iodide
(*b*) isopropyl alcohol and methyl iodide
(*c*) isopropyl alcohol and methyl alcohol
(*d*) isopropyl iodide and methyl alcohol

82. Which one of the following can be oxidised to the corresponding carbonyl compound?

(*a*) *o*-Nitrophenol
(*b*) Phenol
(*c*) 2-methyl-2-hydroxypropane
(*d*) 2-hydroxypropane

83. The reaction which involves dichlorocarbene as an electrophile is

(*a*) Reimer–Tiemann reaction
(*b*) Kolbe's reaction
(*c*) Friedel–Craft's acylation
(*d*) Fittig's reaction

84. Which among the following phenolic compounds is most acidic in nature?

(*a*) *p*-aminophenol
(*b*) phenol
(*c*) *m*-nitrophenol
(*d*) *p*-nitrophenol

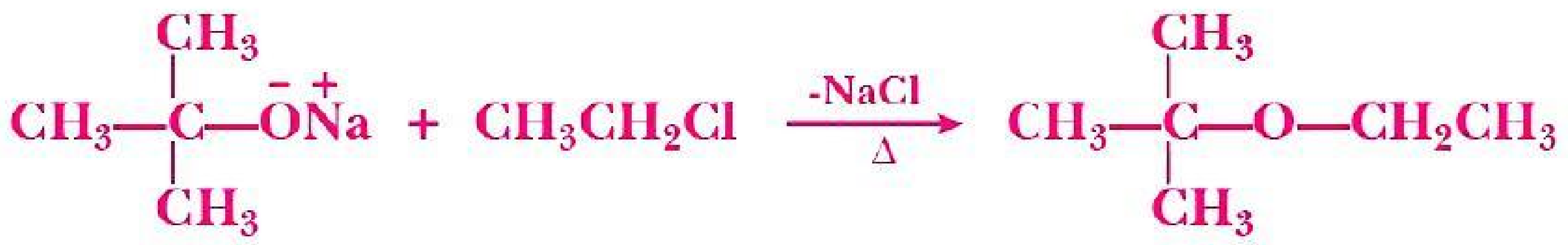
85. In the reaction

$$CH_3COOH \xrightarrow{LiAlH_4} CH_3CH_2OH \xrightarrow{PCl_5} B \xrightarrow{Alc.\ KOH} C$$

The products B and C respectively are

(*a*) Ethyl chloride; Ethene
(*b*) Acetyl chloride; Ethane
(*c*) Ethyl chloride; Acetaldehyde
(*d*) Ethanoyl chloride; Acetaldehyde

86. The reaction



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\overset{-}{O}\overset{+}{Na} + CH_3CH_2Cl \xrightarrow[\Delta]{-NaCl} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2CH_3$$

is called

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

87. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is

(*a*) formation of carbocation.
(*b*) elimination of water.
(*c*) formation of an ester.
(*d*) protonation of an alcohol molecule.

88. The catalyst which is used in commercial method of preparation of phenol is

(*a*) Silica
(*b*) Calcium phosphate
(*c*) Anhydrous aluminium chloride
(*d*) Cobalt naphthenate

89. Arrange the following compounds in the increasing order of their acidic strength:

***i.* *m*-nitrophenol**
***ii.* *m*-cresol**
***iii.* phenol**
***iv.* *o*-chlorophenol**

(*a*) *iii* < *ii* < *i* < *iv*
(*b*) *ii* < *iv* < *iii* < *i*
(*c*) *ii* < *iii* < *iv* < *i*
(*d*) *ii* < *iii* < *i* < *iv*

90. Among the following sets of reactants which one produces anisole?

(*a*) CH_3CHO; RMgX
(*b*) C_6H_5OH; NaOH; CH_3Br
(*c*) C_6H_5OH; neutral $FeCl_3$
(*d*) $C_6H_5—CH_3$; CH_3COCl; $AlCl_3$

91. Select the ether among following that yields methanol as one of the products on reaction with cold hydroiodic acid

(*a*) 1-Methoxybutane
(*b*) 1-Methoxy-2-methylpropane
(*c*) 2-Methoxy-2-methylpropane
(*d*) Methoxybenzene

92. Iodoform can be prepared from all except:

(*a*) Ethyl methyl ketone
(*b*) Isopropyl alcohol
(*c*) 3-Methyl-butan-2-one
(*d*) Isobutyl alcohol

93. Which of the following compounds has highest boiling point?

(*a*) Propan-1-ol (*b*) *n*-Butane (*c*) Chloroethane (*d*) Propanal

94. A liquid was mixed with ethanol and a drop of concentrated H_2SO_4 was added. A compound with a fruity smell was formed. The liquid was

(*a*) HCHO (*b*) CH_3COCH_3 (*c*) CH_3COOH (*d*) CH_3OH

95. Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine?

(*a*) $CH_3CH_2CH(OH)CH_3$ (*b*) CH_3OH
(*c*) CH_3CH_2OH (*d*) $CH_3CH(OH)CH_3$

96. 

$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-\underset{\underset{O}{\|}}{C}-H + CH_3MgBr \xrightarrow{\text{Ether}} A \xrightarrow{H_3O^+} B$$

The IUPAC name of B is

(*a*) Pentan-2-ol (*b*) 2-methylbutan-2-ol
(*c*) 2-methylbutan-3-ol (*d*) 3-methylbutan-2-ol

97. The molecular formula of ether is

(*a*) $C_nH_{2n}O$ (*b*) $C_nH_{2n+1}O$ (*c*) $C_nH_{2n+2}O$ (*d*) $C_nH_{2n}O\ C_nH_{2n}$

98. When Phenyl Magnesium Bromide reacts with tert. butanol, which of the following compound is formed?

(*a*) Tert. butyl methyl ether (*b*) Benzene
(*c*) Tert. butyl benzene (*d*) Phenol

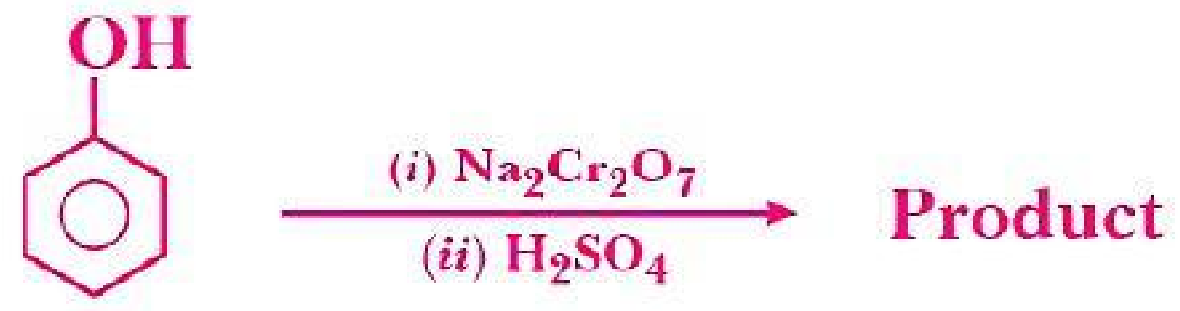
99. Which of the following compounds when heated with CO at 150°C and 500 atm pressure in presence of BF_3 forms ethyl propionate?

(*a*) C_2H_5OH (*b*) CH_3OCH_3 (*c*) $C_2H_5OC_2H_5$ (*d*) $CH_3OC_2H_5$

100. Which of the following conditions are used for the conversion of ethanol to ethylene?

(*a*) dil. H_2SO_4 / 100°C (*b*) dil. H_2SO_4 / 140°C
(*c*) Conc. H_2SO_4 / 70°C (*d*) Conc. H_2SO_4 / 170°C

101. The product of the following reaction is



(*a*) Benzene (*b*) Benzoquinone (*c*) Picric acid (*d*) Salicylaldehyde

102. Which of the following is Lucas reagent?

(*a*) $ZnCl_2$/conc. HCl (*b*) Br_2/CCl_4
(*c*) Ammoniacal silver nitrate (*d*) Cold alkaline $KMnO_4$

103. Which of the following reacts with ethanol to form chloroform?

(*a*) HCl (*b*) PCl_3 (*c*) $SOCl_2$ (*d*) $CaOCl_2/H_2O$

104. Which of the following reagents may be used to distinguish between phenol and benzoic acid?

(*a*) Neutral $FeCl_3$ (*b*) Aqueous NaOH (*c*) Tollen's reagent (*d*) Molisch reagent

105. Which one of the following compounds converts methyl magnesium Iodide to methane in one step?

(*a*) C_2H_4 (*b*) C_2H_5Cl (*c*) $C_2H_5OC_2H_5$ (*d*) C_2H_5OH

106. Two aromatic compounds having formula C_7H_8O which are easily identifiable by $FeCl_3$ solution test(violet colouration) are

(*a*) *o*-cresol and benzyl alcohol (*b*) *m*-cresol and *p*-cresol
(*c*) *o*-cresol and *p*-cresol (*d*) methyl phenyl ether and benzyl alcohol

107. The conversion of *m*-nitrophenol to resorcinol involves respectively

(*a*) diazotization, reduction and hydrolysis
(*b*) hydrolysis, diazotization and reduction
(*c*) reduction, diazotization and hydrolysis
(*d*) hydrolysis, reduction and diazotization

108. An ether is more volatile than an alcohol having the same molecular formula. This is due to

(*a*) dipolar character of ethers.
(*b*) alcohols having resonance structures.
(*c*) inter-molecular hydrogen bonding in ethers.
(*d*) inter-molecular hydrogen bonding in alcohols.

109. The enzymes which are used to convert starch into ethyl alcohol are

(*a*) maltase, diastase
(*b*) diastase, maltase, zymase
(*c*) invertase, zymase
(*d*) invertase, diastase, maltase

110. When benzenesulphonic acid and *p*-nitrophenol are treated with $NaHCO_3$, the gases released respectively are

(*a*) SO_2, NO_2
(*b*) SO_2, NO
(*c*) SO_2, CO_2
(*d*) CO_2, CO_2

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

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

112. *n*-propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent:

(*a*) PCl_5
(*b*) Reduction
(*c*) Oxidation with potassium dichromate
(*d*) Ozonolysis

113. RCH_2CH_2OH can be converted to RCH_2CH_2COOH by the following sequence of steps

(*a*) KNC, H_3O^+
(*b*) PBr_3, KNC, H_2/P^+
(*c*) PBr_3, KCN, H_3O^+
(*d*) HCN, PBr_3, H_3O^+

114. The compound on dehydrogenation gives a ketone. The original compound is

(*a*) tertiary alcohol
(*b*) secondary alcohol
(*c*) primary alcohol
(*d*) carboxylic acid

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

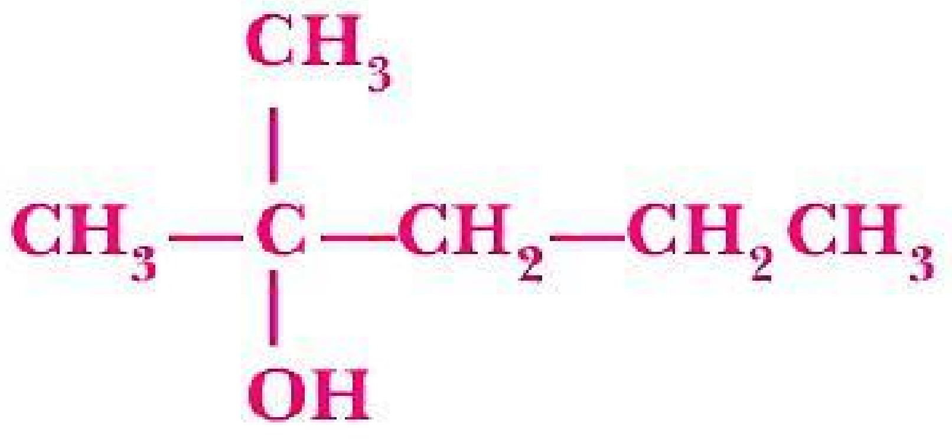
(*a*) HBr
(*b*) conc. H_3PO_4
(*c*) conc. HCl + $ZnCl_2$
(*d*) conc. HCl

116. Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is:

(*a*) 2, 4, 6-tribromophenol
(*b*) 2-bromophenol
(*c*) 3-bromophenol
(*d*) 4-bromophenol

117. Phenol on reaction with CCl_4 in presence of alkali at 340 K produces

(*a*) salicylic acid
(*b*) salicylaldehyde
(*c*) *o*–chlorophenol
(*d*) *p*–chlorophenol

118. The correct IUPAC name of  $CH_3-\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large OH}{|}}{C}}-CH_2-CH_2CH_3$ **[*CBSE 2020 (56/2/1)*]**

(*a*) tert-butyl alcohol
(*b*) 2, 2-Dimethylpropanol
(*c*) 2-Methylpentan-2-ol
(*d*) 3-Methylbutan-3-ol

119. In CH_3—CH_2—OH, the bond that undergoes heterolytic cleavage most readily is

(*a*) C—C
(*b*) C—O
(*c*) C—H
(*d*) O—H

120. An alcohol on oxidation is found to give CH_3COOH and CH_3CH_2COOH. The structure of the alcohol is

(*a*) $CH_3CH_2CH_2OH$
(*b*) $(CH_3)_2C(OH)CH_2—CH_3$
(*c*) $CH_3(CH_2)_3CH_2OH$
(*d*) $CH_3CHOHCH_2CH_2CH_3$

121. Which of the following enzymes converts glucose into ethyl alcohol?

(*a*) Diastase (*b*) Invertase (*c*) Maltase (*d*) Zymase

122. Increasing order of acid strength among *p*-methoxyphenol, *p*-methylphenol, and *p*-nitrophenol is

(*a*) *p*-nitrophenol, *p*-methoxyphenol, *p*-methylphenol

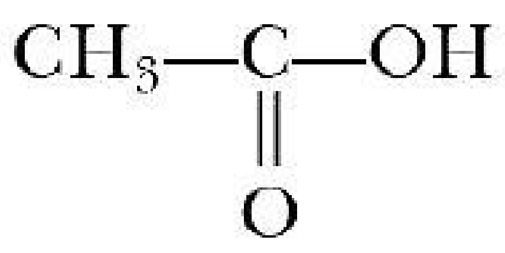
(*b*) *p*-methylphenol, *p*-methoxyphenol, *p*-nitrophenol

(*c*) *p*-nitrophenol, *p*-methylphenol, *p*-methoxyphenol

(*d*) *p*-methoxyphenol, *p*-methylphenol, *p*-nitrophenol.

123. Propan-1-ol may be prepared by the reaction of propene with

(*a*) H_3BO_3 (*b*) $(BH_3)_2$ / NaOH — H_2O_2

(*c*) H_2SO_4 / H_2O (*d*) 

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

124. The correct order of boiling points of for primary(1°), secondary(2°) and tertiary(3°) alcohol is

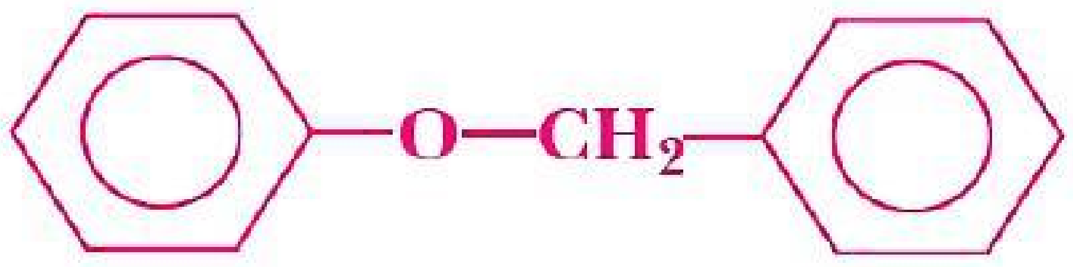
(*a*) 1° > 2° > 3° (*b*) 3° > 2° > 1° (*c*) 2° > 1° > 3° (*d*) 2° > 3° > 1°

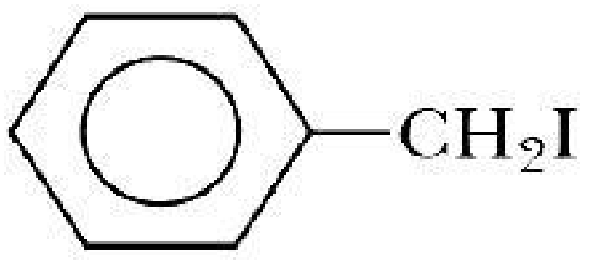
125. For the reaction of phenol with $CHCl_3$ in presence of KOH, the electrophile is

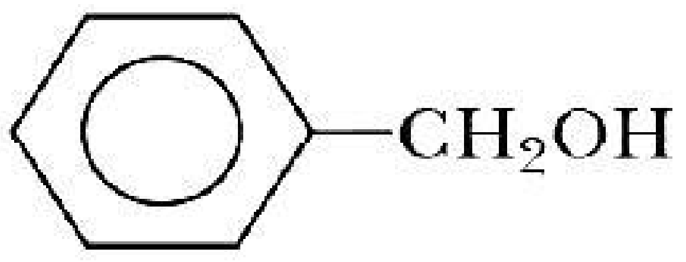
(*a*) $\overset{+}{C}HCl_2$ (*b*) $:CCl_2$ (*c*) $*CHCl_2$ (*d*) None of these

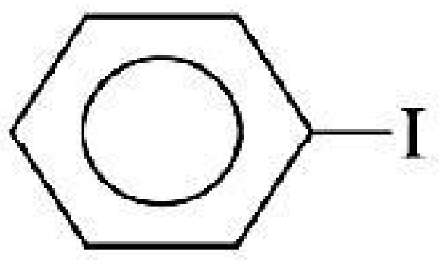
126. The number of optically active stereoisomers are possible for butan-2, 3-diol is

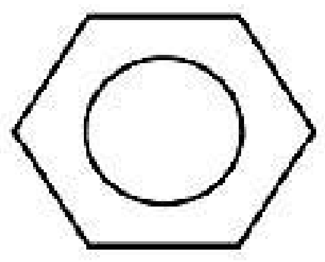
(*a*) 1 (*b*) 2 (*c*) 3 (*d*) 4

127. The ether  **when treated with HI produces :**

(*a*) 

(*b*) 

(*c*) 

(*d*) 

Answers

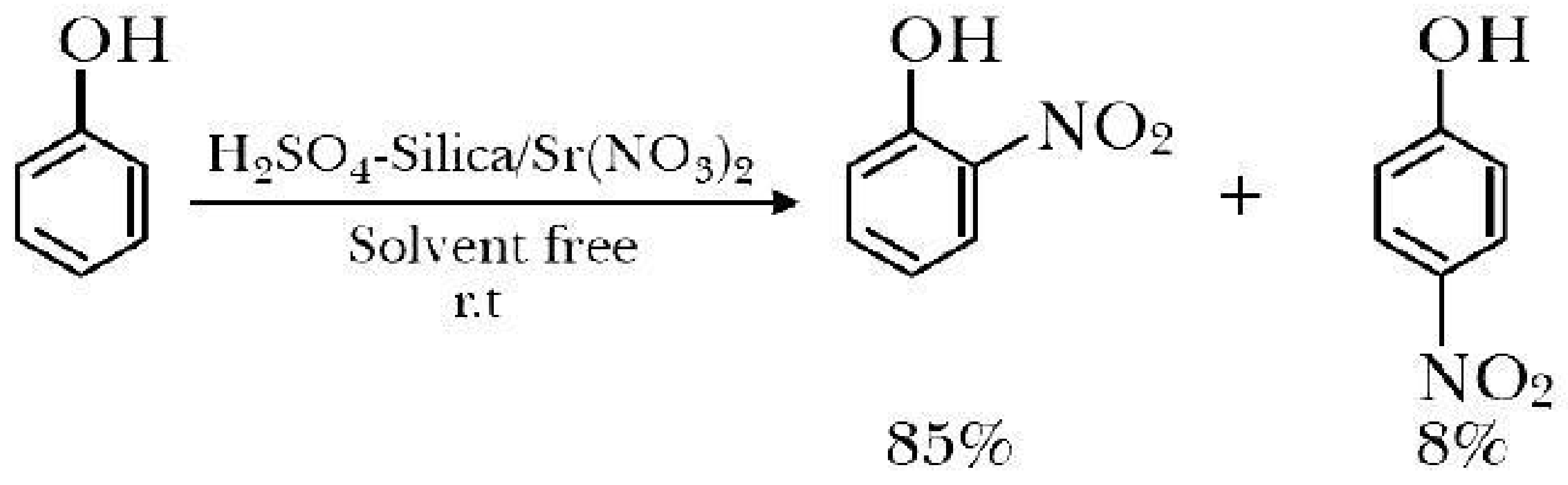
1. (*c*)	**2.** (*a*)	**3.** (*a*)	**4.** (*c*)	**5.** (*d*)	**6.** (*d*)	**7.** (*b*)	**8.** (*b*)
9. (*a*)	**10.** (*b*)	**11.** (*c*)	**12.** (*c*)	**13.** (*c*)	**14.** (*d*)	**15.** (*c*)	**16.** (*d*)
17. (*a*)	**18.** (*d*)	**19.** (*d*)	**20.** (*c*)	**21.** (*b*)	**22.** (*c*)	**23.** (*c*)	**24.** (*b*)
25. (*d*)	**26.** (*c*)	**27.** (*c*)	**28.** (*b*)	**29.** (*b*)	**30.** (*d*)	**31.** (*c*)	**32.** (*b*)
33. (*d*)	**34.** (*b*)	**35.** (*b*)	**36.** (*b*)	**37.** (*c*)	**38.** (*d*)	**39.** (*d*)	**40.** (*b*)
41. (*c*)	**42.** (*c*)	**43.** (*d*)	**44.** (*c*)	**45.** (*b*)	**46.** (*c*)	**47.** (*b*)	**48.** (*a*)
49. (*a*)	**50.** (*c*)	**51.** (*d*)	**52.** (*c*)	**53.** (*d*)	**54.** (*d*)	**55.** (*b*)	**56.** (*d*)
57. (*b*)	**58.** (*d*)	**59.** (*c*)	**60.** (*c*)	**61.** (*b*)	**62.** (*b*)	**63.** (*c*)	**64.** (*d*)
65. (*a*)	**66.** (*b*)	**67.** (*b*)	**68.** (*a*)	**69.** (*a*)	**70.** (*b*)	**71.** (*b*)	**72.** (*a*)
73. (*b*)	**74.** (*d*)	**75.** (*a*)	**76.** (*c*)	**77.** (*b*)	**78.** (*d*)	**79.** (*c*)	**80.** (*a*)
81. (*b*)	**82.** (*d*)	**83.** (*a*)	**84.** (*d*)	**85.** (*a*)	**86.** (*a*)	**87.** (*d*)	**88.** (*d*)
89. (*c*)	**90.** (*b*)	**91.** (*c*)	**92.** (*d*)	**93.** (*a*)	**94.** (*c*)	**95.** (*b*)	**96.** (*d*)
97. (*c*)	**98.** (*b*)	**99.** (*c*)	**100.** (*d*)	**101.** (*b*)	**102.** (*a*)	**103.** (*d*)	**104.** (*a*)
105. (*d*)	**106.** (*a*)	**107.** (*c*)	**108.** (*d*)	**109.** (*b*)	**110.** (*d*)	**111.** (*a*)	**112.** (*c*)
113. (*c*)	**114.** (*b*)	**115.** (*b*)	**116.** (*a*)	**117.** (*a*)	**118.** (*c*)	**119.** (*d*)	**120.** (*d*)
121. (*d*)	**122.** (*d*)	**123.** (*b*)	**124.** (*a*)	**125.** (*b*)	**126.** (*b*)	**127.** (*a*)	

CASE-BASED QUESTIONS

1. Read the passage given below and answer the following questions:

Nitration of phenols is an important process, because nitrophenols are important intermediates for the manufacture of drugs and pharmaceuticals. But phenols are highly reactive; therefore the nitration of phenols using the classical method of nitric acid in sulphuric acid generally gives complex mixtures containing o-and p-nitrophenols, dinitrated phenols and unextractable tars of phenolic oxidation products. Regioselective nitration of phenol to furnish ortho and para-nitrophenol as special cases has been studied by various nitrating agents under different conditions. However, some of the nitrating reagents are poorly regioselective and uneconomical. On the other hand, considering these concerns, there is still a good scope for research towards finding mild reagents for regioselective nitration of phenols.

Recently, the use of catalysts and reagents supported on solid supports and solvent-free conditions was developed because such reagents not only simplify the purification processes but also help to prevent the releasing of toxic reaction residues such as excess acid or the corresponding salt of acid into the environment. Regioselective nitration of phenols using $Sr(NO_3)_2$ or benzyltriphenylphosphonium nitrate in the presence of H_2SO_4-silica had been realized under solvent free conditions. The reaction proceeds through the formation of nitronium ion, which attack the phenol ring preferential at ortho position in presence of $Sr(NO_3)_2$, forming mono-nitrophenol. Para-orientation relative to hydroxyl group and mononitration of phenolic compounds was observed in the case of benzyltriphenylphosphonium nitrate. Some of the major advantages of this method are mild reaction conditions, high efficiency and regioselectivity of nitration and complementarity with other reported methods. In addition, benzyltriphenylphosphonium nitrate as nitrating reagent can be easily recycled.



Regioselective nitration of phenol by $Sr(NO_3)_2$

(***Reference:*** *School of Chemistry, Damghan University, Damghan—Iran*)

The following questions are multiple choice questions. Choose the most appropriate answer:

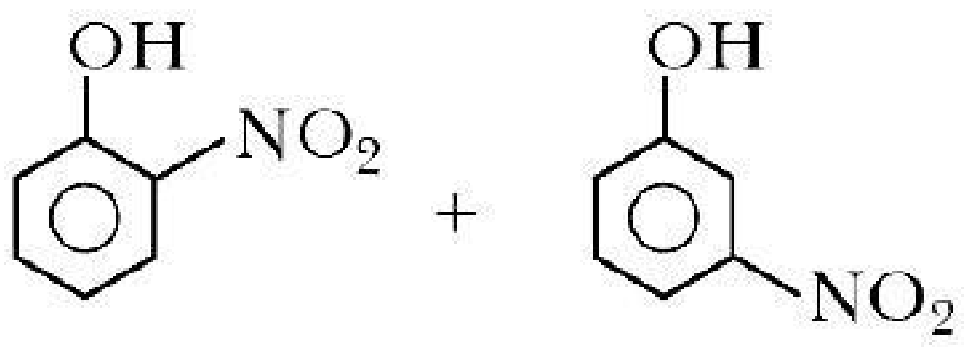
(*i*) Phenols undergo nitration in concentrated nitric acid to produce

(*a*) dinitrophenol (*b*) nitrophenol (*c*) tetranitrophenol (*d*) trinitrophenol

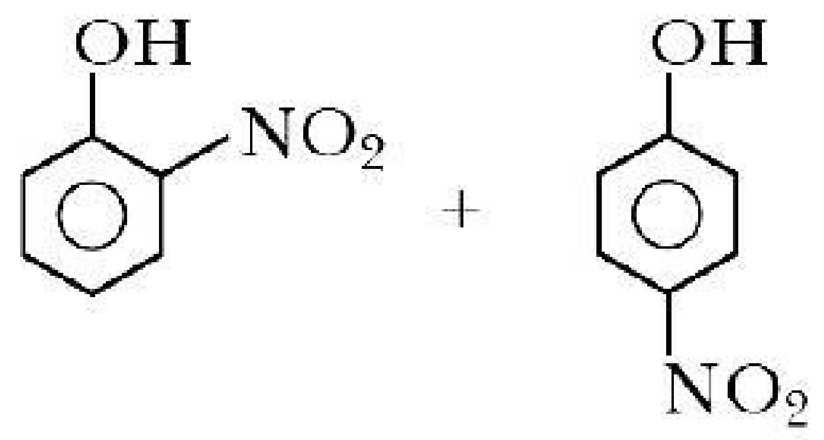
(*ii*) Identify the products formed in the given reaction

+ HNO_3 (dil.) $\longrightarrow$

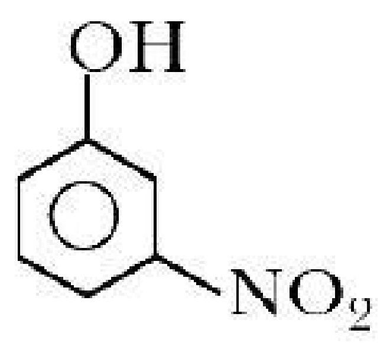
(*a*)



(*b*)

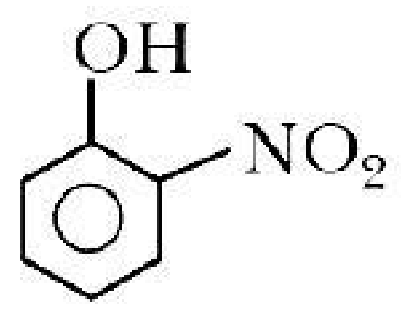


(*c*)



+ H_2O

(*d*)



+ H_2O

OR

Which of the following statements is correct about nitration of phenol?

(*a*) HNO_3 is an electrophile.

(*b*) HNO_3 is a nucleophile.

(*c*) Benzene ring is an electrophile.

(*d*) HNO_3 and Benzene ring both are electrophile.

(*iii*) **Phenol can be easily nitrated because of**

(*a*) presence of OH group that increases electron density on *o* and *p*-position.

(*b*) presence of OH group that decreases electron density on *o* and *p*-position.

(*c*) presence of OH group that increases electron density on *m*-position.

(*d*) HNO_3 is strongest oxidising agent.

(*iv*) **In nitration of phenol by dil. HNO_3, *o*-nitrophenol is steam volatile because**

(*a*) it possess intramolecular hydrogen bonding.

(*b*) it possess intermolecular hydrogen bonding.

(*c*) *p*-nitrophenol is more stable than o-nitrophenol.

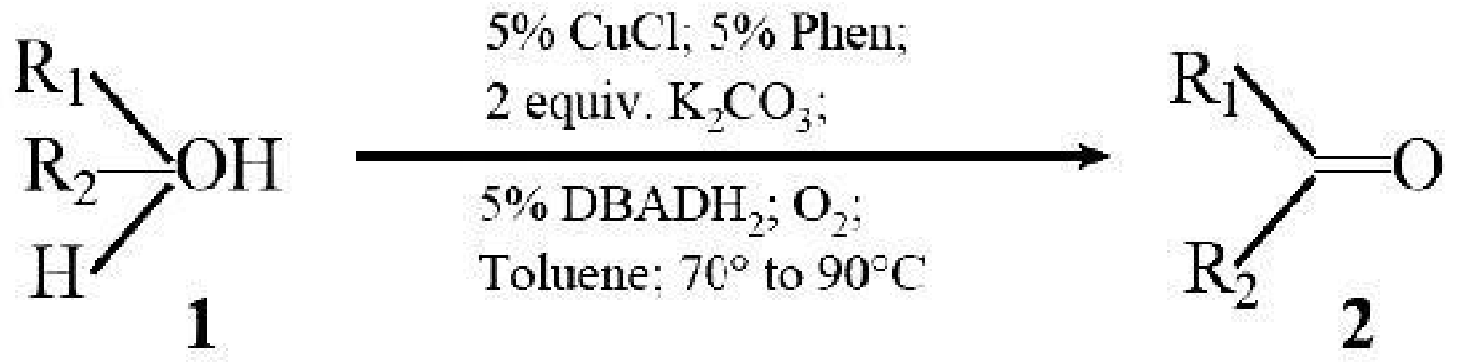
(*d*) none of the above is correct statement.

Answers

(*i*) (*d*) (*ii*) (*b*) (*iii*) (*a*) (*iv*) (*a*)

2. Read the passage given below and answer the following questions:

An efficient, aerobic catalytic system for the transformation of alcohols into carbonyl compounds under mild conditions, copper-based catalyst has been discovered. This copper-based catalytic system utilizes oxygen or air as the ultimate, stoichiometric oxidant, producing water as the only by-product



A wide range of primary, secondary, allylic, and benzylic alcohols can be smoothly oxidized to the corresponding aldehydes or ketones in good to excellent yields. Air can be conveniently used instead of oxygen without affecting the efficiency of the process. However, the use of air requires slightly longer reaction times.

This process is not only economically viable and applicable to large-scale reactions, but it is also environmentally friendly.

(***Reference:*** *Ohkuma, T., Ooka, H., Ikariya, T., & Noyori, R. (1995). Preferential hydrogenation of aldehydes and ketones. Journal of the American Chemical Society, 117(41), 10417-10418.*)

The following questions are multiple choice questions. Choose the most appropriate answer:

(*i*) **The Copper based catalyst mention in the study above can be used to convert:**

(*a*) propanol to propanonic acid (*b*) propanone to propanoic acid

(*c*) propanone to propan-2-ol (*d*) propan-2-ol to propanone

(*ii*) **The carbonyl compound formed when ethanol gets oxidised using this copper-based catalyst can also be obtained by ozonolysis of:**

(*a*) But-1-ene (*b*) But-2-ene (*c*) Ethene (*d*) Pent-1-ene

(*iii*) Benzyl alcohol on treatment with this copper-based catalyst gives a compound 'A' which on reaction with KOH gives compounds 'B' and 'C'. Compound 'B' on oxidation with $KMnO_4$-KOH gives compound 'C'. Compounds 'A', 'B' and 'C' respectively are:

(*a*) Benzaldehyde, Benzyl alcohol, potassium salt of Benzoic acid

(*b*) Benzaldehyde, potassium salt of Benzoic acid, Benzyl alcohol

(*c*) Benzaldehyde, Benzoic acid, Benzyl alcohol

(*d*) Benzoic acid, Benzyl alcohol, Benzaldehyde

(*iv*) An organic compound 'X' with molecular formula C_3H_8O on reaction with this copper based catalyst gives compound 'Y' which reduces Tollen's reagent. 'X' on reaction with sodium metal gives 'Z'. What is the product of reaction of 'Z' with 2-chloro-2-methylpropane?

(*a*) $CH_3CH_2CH_2OC(CH_3)_3$ (*b*) $CH_3CH_2OC(CH_3)_3$

(*c*) $CH_2{=}C(CH_3)_2$ (*d*) $CH_3CH_2CH{=}C(CH_3)_2$

Answers

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

ASSERTION-REASON QUESTIONS

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

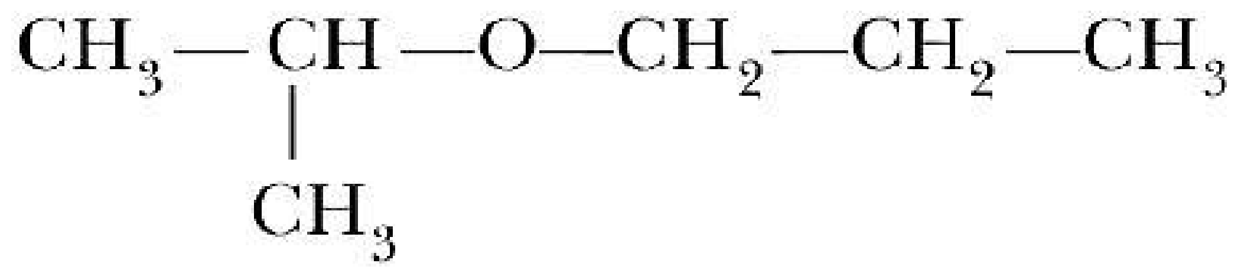
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

1. **Assertion (A) :** IUPAC name of the compound



$CH_3—\underset{\displaystyle CH_3}{\underset{|}{CH}}—O—CH_2—CH_2—CH_3$ is 2-Ethoxy-2-methylethane.

Reason (R) : In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by —OR or —OAr group [where R = alkyl group and Ar = aryl group].

2. **Assertion (A) :** The boiling point of ethanol is higher than methoxymethane.

Reason (R) : There is intramolecular hydrogen bonding in ethanol.

3. **Assertion (A) :** Ethanol is a weaker acid than phenol.

Reason (R) : Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

4. **Assertion (A) :** *o*-Nitrophenol is less soluble in water than the *m*- and *p*-isomers.

Reason (R) : *m*- and *p*- Nitrophenols exist as associated molecules.

5. **Assertion (A) :** *p*-nitrophenol is more acidic than phenol.

Reason (R) : Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

6. **Assertion (A) :** In lucas test, 3° alcohols react immediately.

Reason (R) : An equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl is called Lucas reagent.

7. **Assertion (A) :** Phenol on oxidation with chromic acid gives benzoquinone.

Reason (R) : Pure phenol is colourless but turn pink due to oxidation to phenoquinone.

8. **Assertion (A) :** Phenol is more reactive than benzene towards electrophilic substitution reaction.

Reason (R) : In the case of phenol, the intermediate carbocation is more resonance stabilized.

9. Assertion (A) : Phenols give *o*- and *p*-nitrophenol on nitration with conc. HNO_3 and H_2SO_4 mixture.

Reason (R) : —OH group in phenol is *o*–, *p*– directing.

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

Reason (R) : Lewis acid polarises the bromine molecule.

11. Assertion (A) : The reaction of phenol with acid chloride to form ether occurs in the presence of pyridine.

Reason (R) : Pyridine is a base so it neutralises the HCl formed and proceeds the reaction.

12. Assertion (A) : Bond angle in ethers is slightly less than the tetrahedral angle.

Reason (R) : There is a repulsion between the two bulky (—R) groups.

13. Assertion (A) : *o*-nitrophenol is a weaker acid than p-nitrophenol. *[CBSE 2020 (56/2/1)]*

Reason (R) : Intramolecular hydrogen bonding makes ortho isomer weaker than para isomer.

14. Assertion (A) : The C–O–H bond angle in alcohols is slightly less than the tetrahedral angle. *[CBSE 2020 (56/3/1)]*

Reason (R) : This is due to the repulsive interaction between the two lone election pairs on oxygen.

15. Assertion (A) : Phenol is more acidic than *p*-methylphenol. *[CBSE 2020 (56/3/2)]*

Reason (R) : The presence of an electron releasing group in *p*-methylphenol makes it less acidic.

16. Assertion (A) : $(CH_3)_3$ C—O—CH_3 gives $(CH_3)_3$ C—I and CH_3OH on treatment with HI. *[CBSE 2020 (56/4/1)]*

Reason (R) : The reaction occurs by S_N1 mechanism.

17. Assertion (A) : The C–O–C bond angle in ethers is slightly less than tetrahedral angle. *[CBSE 2020 (56/5/1)]*

Reason (R) : Due to the repulsive interaction between the two alkyl groups in ethers.

18. Assertion (A) : Ortho and para-nitrophenols can be separated by steam distillation. *[CBSE 2020 (56/5/2)]*

Reason (R) : Ortho isomer associates through intermolecular hydrogen bonding while Para isomer associates through intramolecular hydrogen bonding.

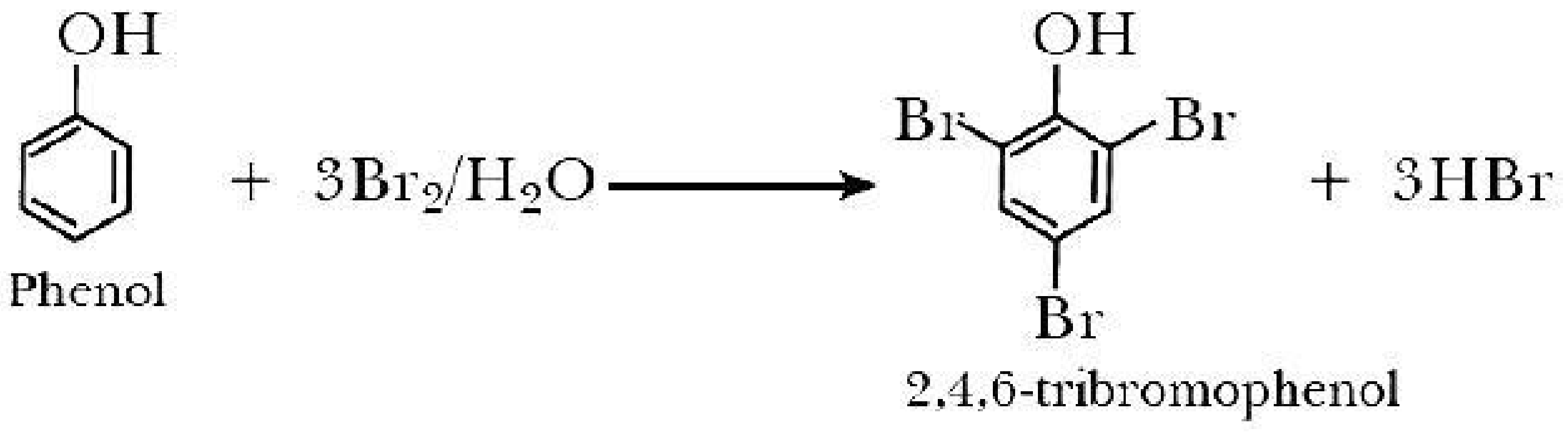
Answers

1. (*d*) **2.** (*c*) **3.** (*c*) **4.** (*b*) **5.** (*a*) **6.** (*b*) **7.** (*b*) **8.** (*a*)
9. (*d*) **10.** (*d*) **11.** (*d*) **12.** (*d*) **13.** (*a*) **14.** (*a*) **15.** (*a*) **16.** (*a*)
17. (*d*) **18.** (*c*)

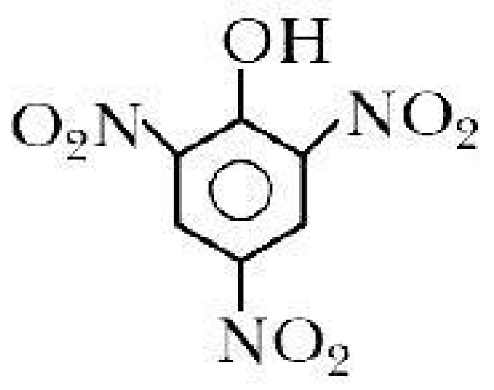
HINTS/SOLUTIONS OF SELECTED MCQS

1. (*c*) Aromatic alcohols are compounds in which -OH group is not directly attached with benzene ring directly.

22. (*c*)

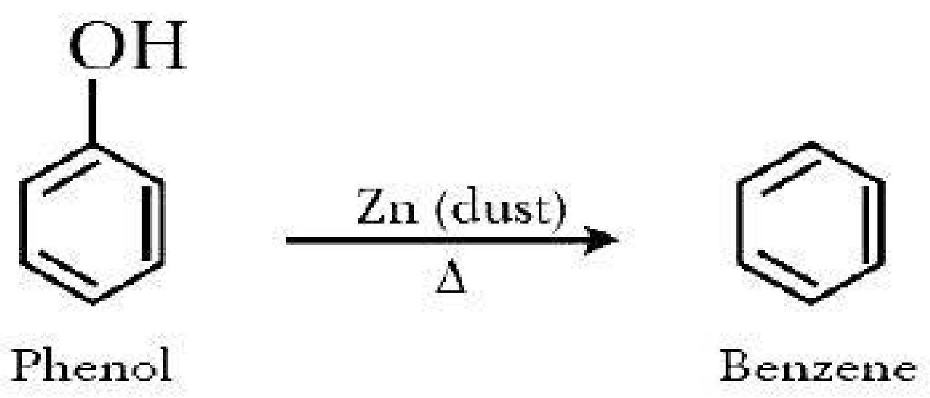


23. (*c*) The structure of picric acid is



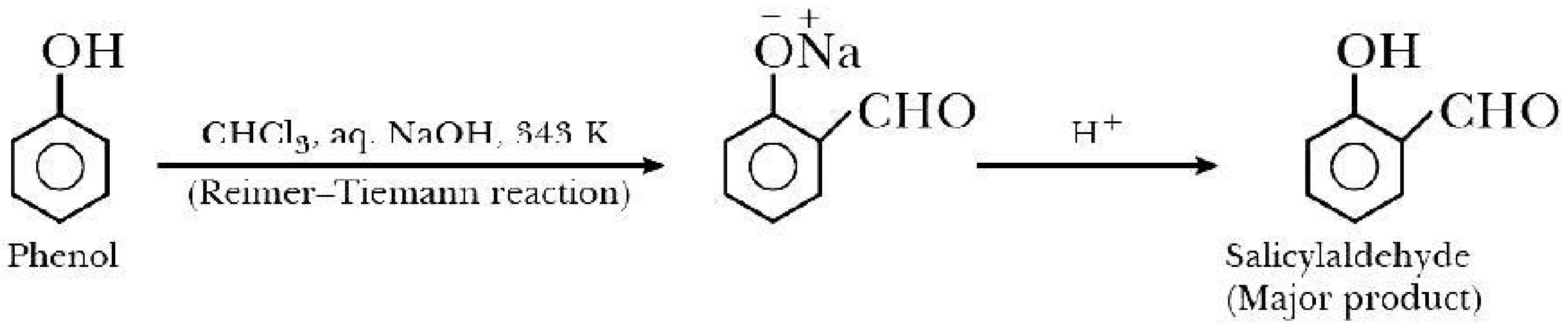
2,4,6-trinitrophenol

24. (*b*)



25. (*d*) Most ring activators have atoms with unshared electron pairs directly attached to a carbon atom of the benzene ring. For example, the —OH group has two pairs of unshared electrons on the oxygen atom, which will form a bond to a carbon atom of the benzene ring. Thus, the —OH group will be an activating group.

26. (*c*)



Note: A small amount of *p*-hydroxybenzaldehyde is also formed.

27. (*c*) Phenol is also known as carbolic acid.

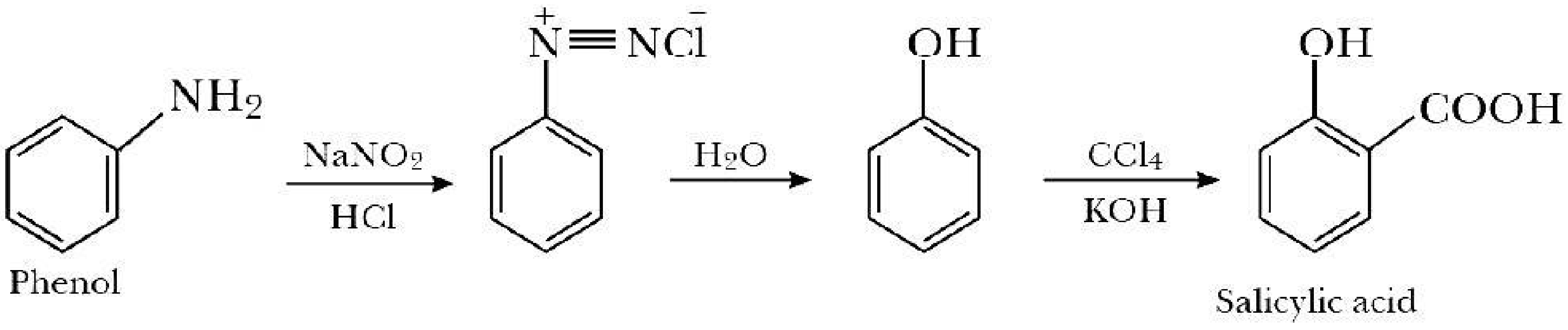
28. (*b*) Phenol gives a violet-coloured water soluble complex with ferric chloride while benzyl alcohol does not react with $FeCl_3$.

$$6C_6H_5OH + FeCl_3 \xrightarrow{373\text{ K}} \underset{\text{Violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

Phenol

In general, all compounds containing phenolic group $(=\overset{|}{C}-OH)$ respond to this test. However, the colours of complexes are different such as green, blue, violet, etc., and depend upon the structure of phenols.

29. (*b*)



30. (*d*) The general formula of monohydric alcohol is $C_nH_{2n+1}OH$ where $n = 1, 2, 3....$etc.

31. (*c*) Primary alcohols are those alcohols in which the -OH group is attached to a primary carbon atom.

32. (*b*) Secondary alcohols are those alcohols in which the -OH group is attached to a secondary carbon atom.

33. (*d*) Ethane 1, 2-diol is an example of dihydric alcohol because it contains two hydroxyl group.

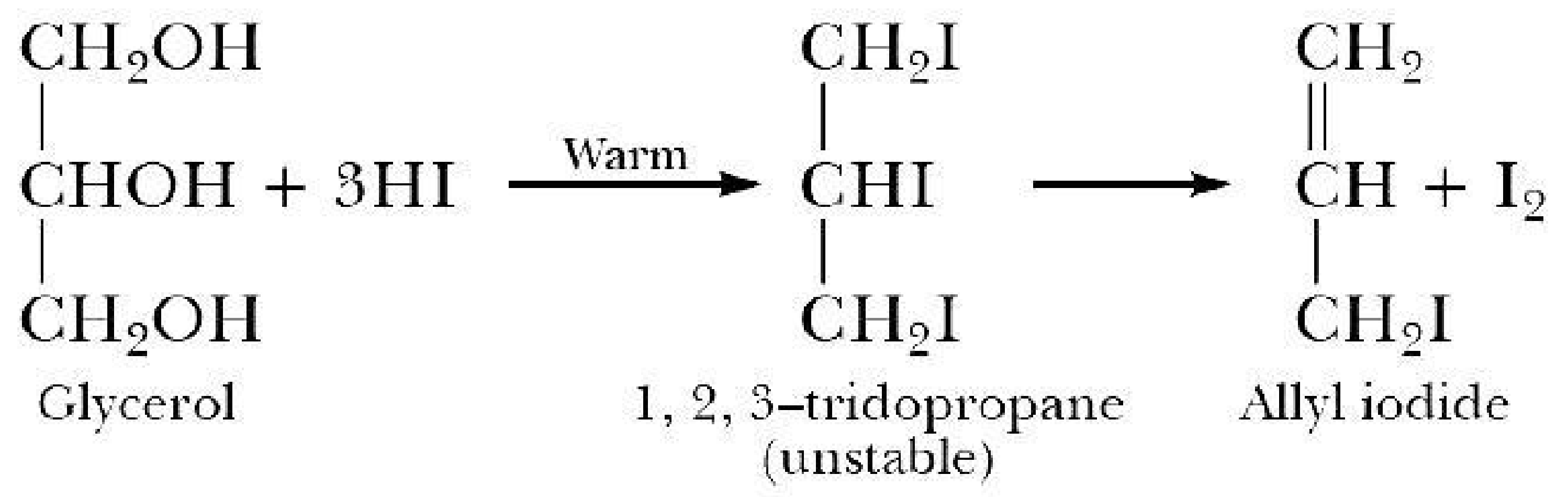
34. (*b*) Butan-2-ol is a secondary alcohol because in this -OH group is attached to secondary carbon atom.

35. (*b*) Butan-1-ol is a primary alcohol because in this -OH group is attached to primary carbon atom.

36. (*b*) The solubility of lower alcohols in water is due to their ability to form hydrogen bonds with water molecules. The solubility of alcohols in water decreases with increase in molecular mass because with increase in molecular mass the non-polar alkyl group becomes predominant and masks the effect of polar —OH group. In addition, among the isomeric alcohols the solubility increases with branching of chain. It is because the surface area of non-polar part in the molecule decreases, thus enhancing the solubility.

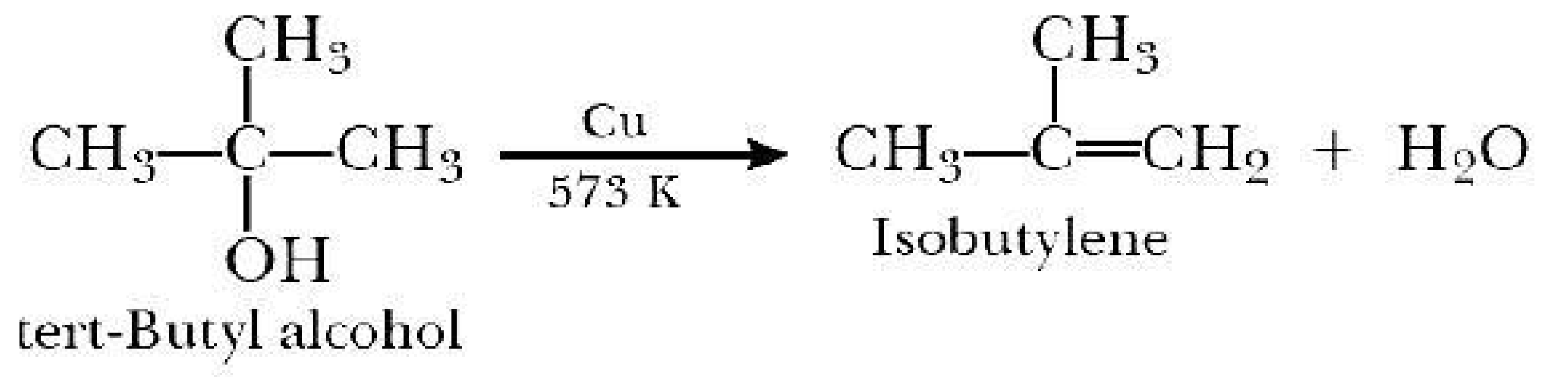
37. (*c*) When a mixture of methyl alcohol and air is passed through a heated tube containing iron powder and molybdenum oxide, methanal is formed.

38. (*d*)



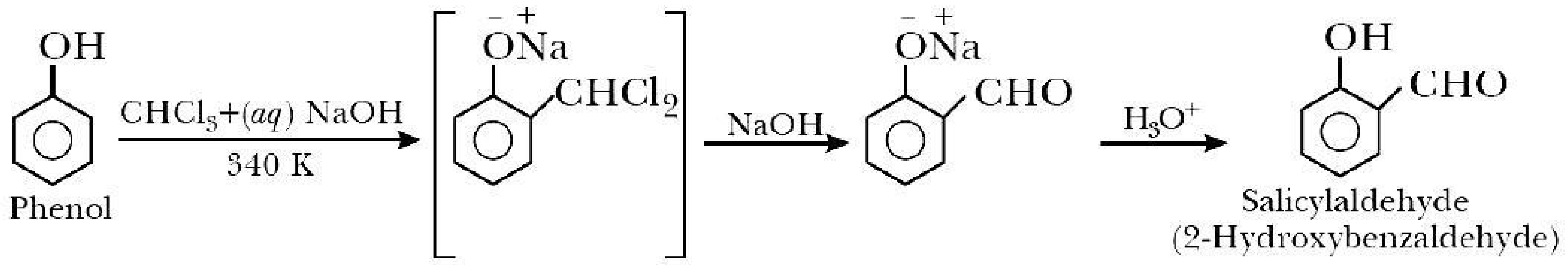
$$\underset{\text{Glycerol}}{\begin{array}{c}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{array}} + 3HI \xrightarrow{\text{Warm}} \underset{\substack{\text{1, 2, 3–tridopropane}\\\text{(unstable)}}}{\begin{array}{c}CH_2I\\|\\CHI\\|\\CH_2I\end{array}} \longrightarrow \underset{\text{Allyl iodide}}{\begin{array}{c}CH_2\\\|\\CH\\|\\CH_2I\end{array}} + I_2$$

39. (*d*) Tertiary alcohols undergo dehydration to give alkenes.



$$\underset{\text{tert-Butyl alcohol}}{CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}—CH_3} \xrightarrow[573\text{ K}]{\text{Cu}} \underset{\text{Isobutylene}}{CH_3—\overset{\overset{CH_3}{|}}{C}=CH_2} + H_2O$$

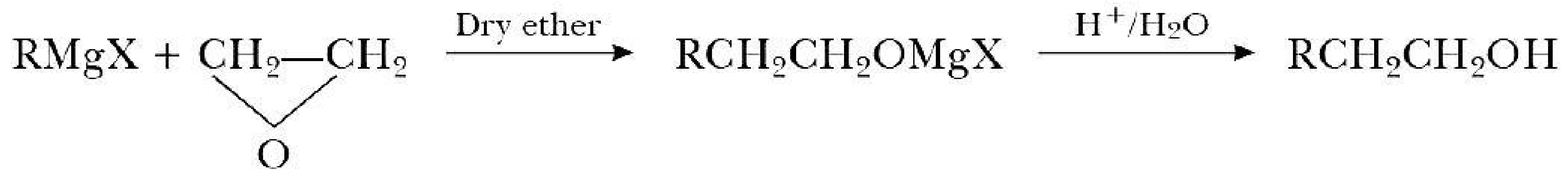
40. (*b*) Reimer–Tiemann reaction: Treatment of phenol with chloroform in the presence of sodium hydroxide followed by hydrolysis of resulting product gives o-hydroxybenzaldehyde(salicylaldehyde) as a major product.



41. (*c*) $\underset{\text{Ethyl alcohol}}{CH_3—CH_2—OH} \xrightarrow[443\text{ K}]{H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$

42. (*c*) Phenol and ethanol both can react with sodium and gives sodium phenoxide and sodium ethoxide respectively.

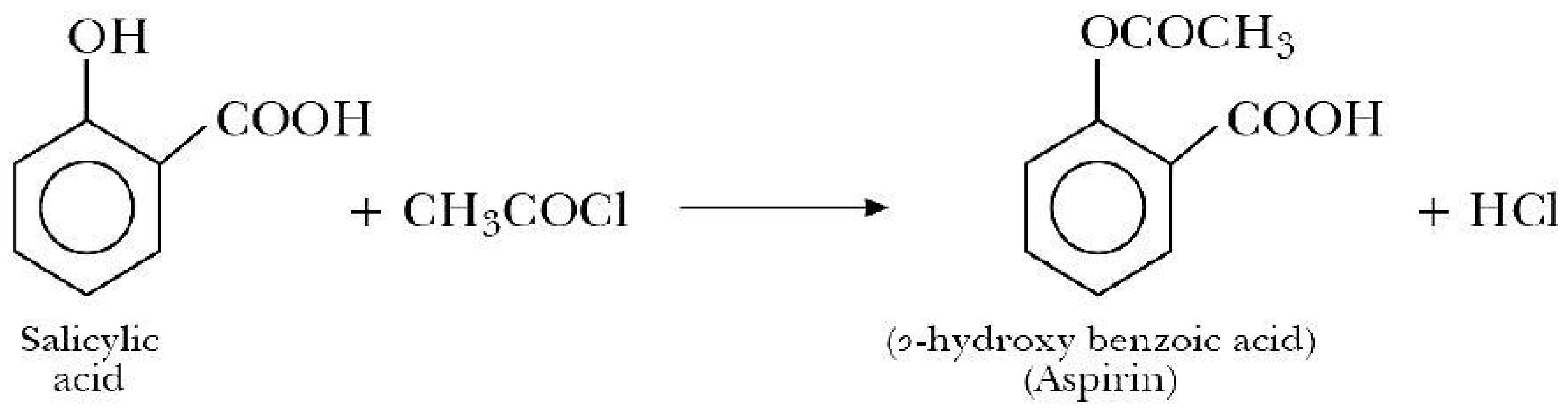
43. (*d*)



$$RMgX + \underset{\diagdown\ O\ \diagup}{CH_2—CH_2} \xrightarrow{\text{Dry ether}} RCH_2CH_2OMgX \xrightarrow{H^+/H_2O} RCH_2CH_2OH$$

44. (*c*) —OH, —Cl and —CH_3 groups in benzene are ortho-para directing groups and activate the ring towards electrophilic substitution reaction. But among these —OH group is strongly activating while —CH_3 is weakly activating and —Cl is deactivating. Thus, phenol will be most easily attacked by an electrophile.

45. (*b*) Aspirin(2-acetoxy benzoic acid) is an acetylated product of salicylic acid.



46. (*c*) The C—O bonds are polar in ether and therefore they have a net dipole moment.

47. (*b*) Phenoxide ion is more stable than ethoxide ion due to resonance. Therefore, the ionisation constant of phenol is higher than ethanol.

48. (*a*) Steam distillation is the most suitable method of separation of 1:1 mixture of ortho and para nitrophenols as there is intramolecular H-bonding in ortho nitrophenol due to which it is steam volatile *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding.

49. (*a*) $3CH_2 = CH_2 \xrightarrow{B_2H_6} (CH_3CH_2)_3B \xrightarrow[H_2O]{3H_2O_2,\ OH^-} 3CH_3CH_2OH$

Hydroboration oxidation of alkenes leads to hydration in anti-Markownikoffs way.

50. (*c*) Due to the presence of Chlorine atom in a compound such as *o*-chlorophenol, it is considered as most acidic than phenol, benzyl alcohol, and cyclohexanol.

It is because, as chlorine is an electron loving element it facilitates delocalization of negative charge in phenoxide ion.

51. (*d*) $Mg + C_2H_5OH \longrightarrow Mg(OC_2H_5)_2 + H_2$

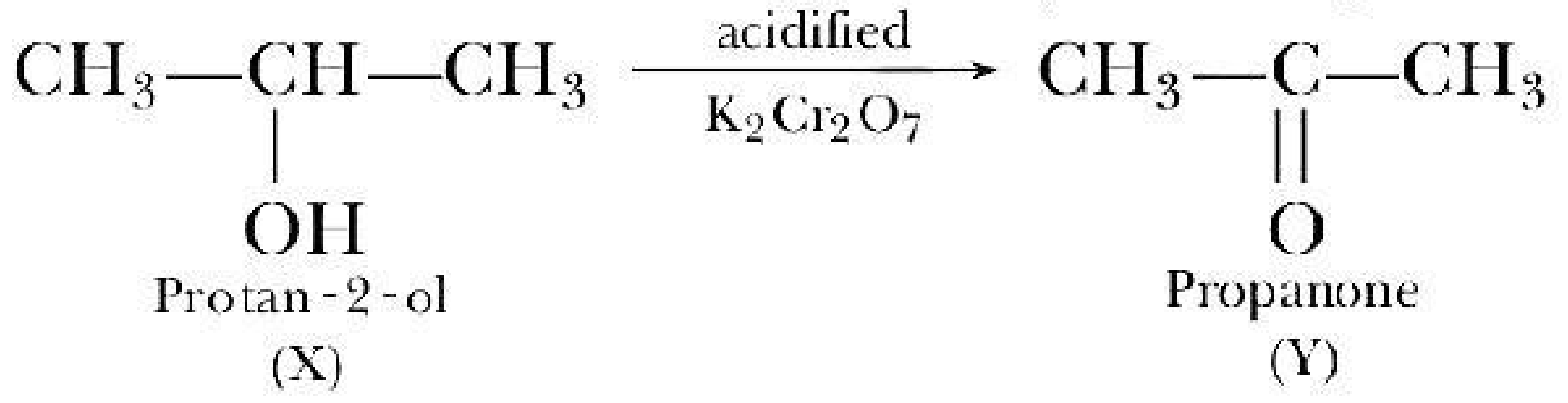
$Mg(OC_2H_5)_2 + H_2O \longrightarrow MgO + 2C_2H_5OH$

52. (*c*) 2,4,6-trinitrophenol, benzoic acid and benzene sulphonic acid are soluble in $NaHCO_3$. This reaction is possible in the forward direction if acid is more acidic than H_2CO_3. *o*-nitrophenol is less acidic than H_2CO_3. Hence, it is not soluble in $NaHCO_3$.

53. (*d*) The compound Y must contain $CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—$ or $CH_3CO—$ as it is responding to iodoform test.

Among the given compounds, $CH_3CHOHCH_3$ (a secondary alcohol) on treatment with acidified $K_2Cr_2O_7$ gives $CH_3—\underset{\displaystyle O}{\underset{||}{C}}—CH_3$ (a ketone with $—CH_3CO$ group).

Therefore, X and Y respectively are $CH_3CHOHCH_3$ and CH_3COCH_3.



$$\underset{\text{(X)}}{\underset{\text{Protan-2-ol}}{CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3}} \xrightarrow[K_2Cr_2O_7]{\text{acidified}} \underset{\text{(Y)}}{\underset{\text{Propanone}}{CH_3—\underset{\displaystyle O}{\underset{||}{C}}—CH_3}}$$

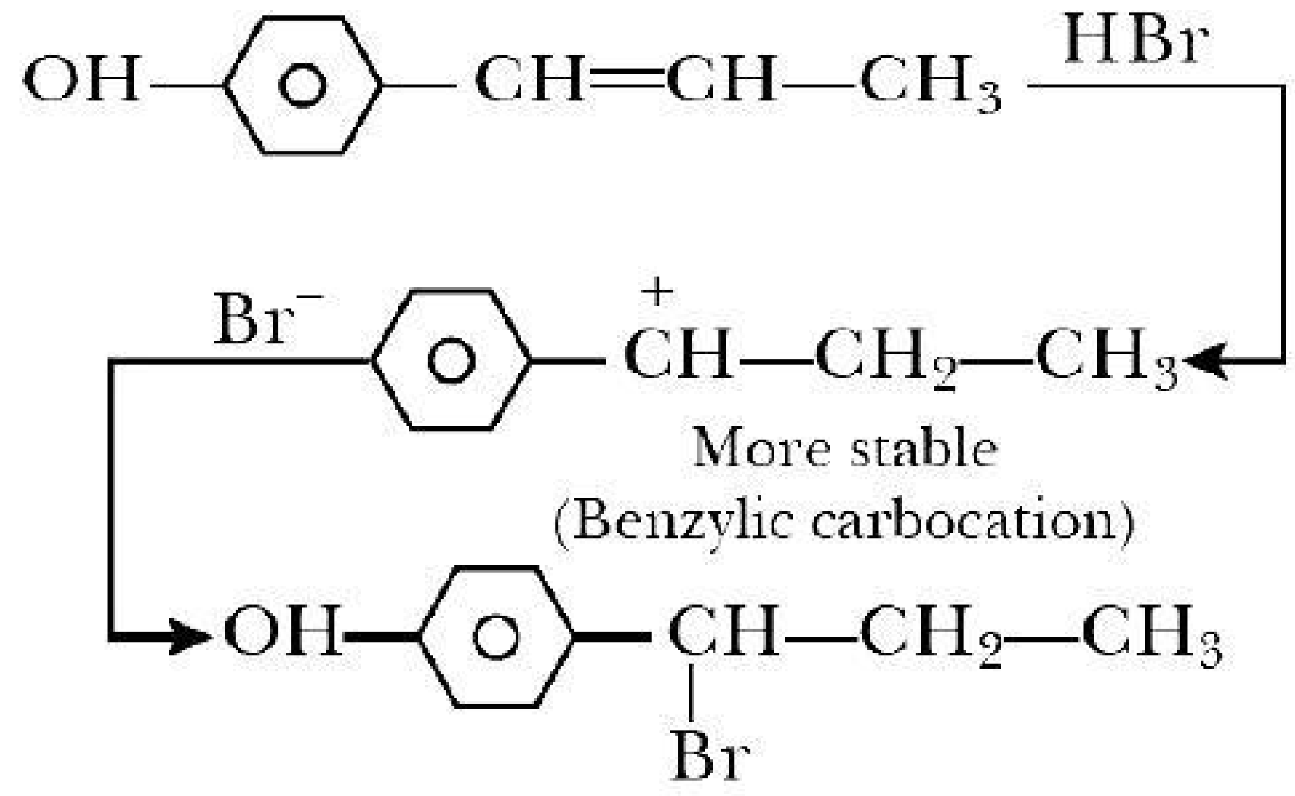
54. (*d*) Presence of electron withdrawing groups such as nitro group enhance the acidic strength of phenol and the presence of electron releasing groups such as alkyl group decreases the acidic strength of phenol.

As NO_2 group at *p*-position withdraws electrons towards itself by stronger —R effect as compared to $—NO_2$ group at *m*-position which withdraws electrons by the weaker —I effect. Thus, *p*-nitrophenol is more acidic than *m*-nitrophenol.

55. (*b*) The presence of —OH group activates the benzene ring towards electropilic substitution reaction and directs the incoming group at *o* and *p*- positions as these positions become electron rich due to the resonance effect.

56. (*d*) Iodoform test is given by the compounds containing terminal $CH_3CO—$ and $CH_3CH(OH)—$ group Thus it is given by compound (*d*) only. Since only (*d*) contains alpha hydroxyl group and moreover, it is not given by acid derivatives.

57. (*b*) This is due to formation of benzylic carbocation as an intermediate which is stabilized by resonance.



58. (*d*) The strongest acid is CH_3OH, because the bond O—H is strongly polarized due to large electronegativity difference between oxygen and hydrogen. Moreover, on loosing a proton, $CH_3—O^{\ominus}$ is stabilized.

For the rest examples, the C—H bonds are less polarized, and only ethyne is less acidic than methanol due to low electronegativity of carbon as compared to oxygen in CH_3OH. The rest cases (benzene, and ethane) are not acidic.

59. (*c*) Diethyl ether on heating with conc. HI gives ethyl iodide.

$$CH_3CH_2OCH_2CH_3 + 2HI \rightarrow 2CH_3CH_2I + H_2O$$

60. (*c*) Though ethyl alcohol and dimethyl ether have the same molecular weight but in ethyl alcohol the hydrogen of the —OH group forms intermolecular hydrogen bonding with the —OH group in another molecule. But in case of ether, the hydrogen is linked to C and it is not so electronegative to encourage the hydrogen to form hydrogen bonding. Due to intermolecular H-bonding, ethyl alcohol remains in the associated form and therefore, boils at a higher temperature compared to dimethyl ether.

61. (*b*) The Williamson's synthesis is the most widely used method to produce ethers. It occurs by an S_N2 reaction in which a metal alkoxide displaces a halide ion from an alkyl halide. The alkoxide ion is prepared by the reaction of an alcohol with a strong base such as sodium hydride.

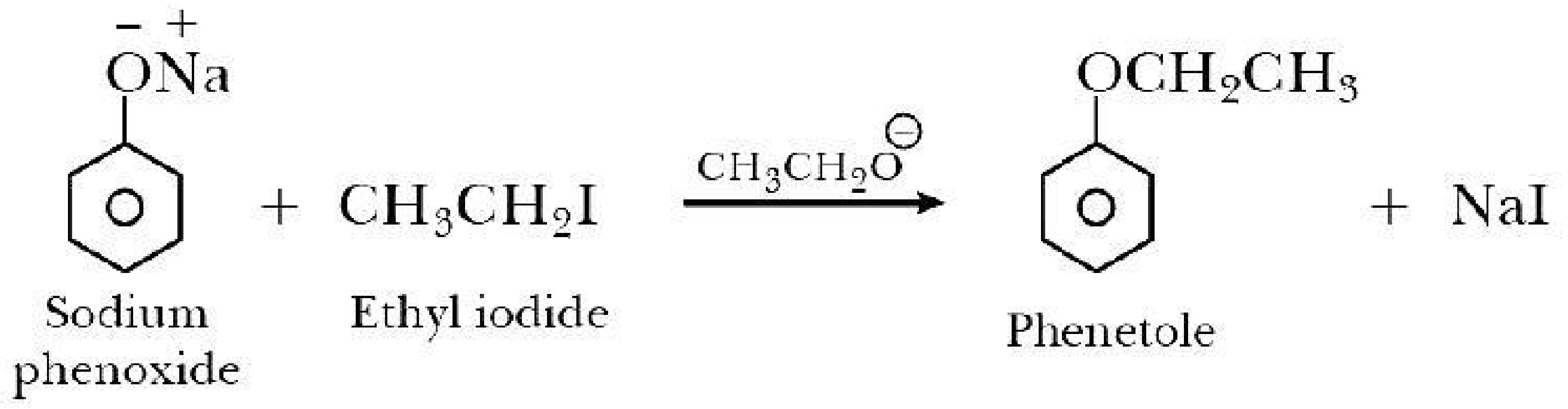
62. (*b*) The Williamson's synthesis is the most widely used method to produce ethers. It occurs by an S_N2 reaction in which a metal alkoxide displaces a halide ion from an alkyl halide. The alkoxide ion is prepared by the reaction of an alcohol with a strong base such as sodium hydride.

63. (*c*) Diethyl ether is formed by the acid catalysed dehydration reaction of ethanol and conc. sulphuric acid by the loss of water molecule. Conc. sulphuric acid used as catalyst, as well as a dehydrating agent.

$$\underset{\substack{\text{Ethanol}\\ \text{(excess)}}}{2C_2H_5OH} + H_2SO_4 \xrightarrow{413\text{ K}} \underset{\text{Ethoxyethane}}{C_2H_5—O—C_2H_5} + H_2O$$

64. (*d*) The formula of diethylether is $C_2H_5OC_2H_5$.

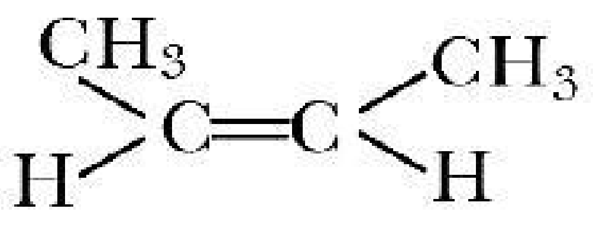
65. (*a*)



66. (*b*) Here, the compound 'Z' formed is either but-1-ene(minor) or but-2-ene(major).

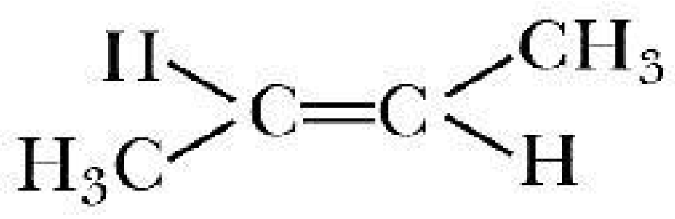
Thus, there are three structures possible.

1.



cis-but-2-ene

2.



trans-but-2-ene

3. $CH_3—CH_2—CH═CH_2$

But-1-ene

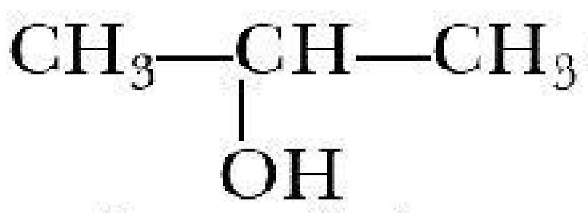
67. (*b*) The order of boiling point is as follow

R—COOH > R—OH > R—CHO

This is because carboxylic acid forms dimer due to formation of extensive intermolecular hydrogen bonding. As we know that more is the extend of hydrogen bonding more is the boiling point. Also, alcohol contains hydrogen bonding but is not a dimer and aldehyde or ketone does not possess hydrogen bonding.

68. (*a*) $\underset{\text{Propan-1-ol}}{CH_3—CH_2—CH_2OH} \xrightarrow[\Delta,\ 300°C]{Cu} CH_3—CH_2—CHO$

$\xrightarrow[\text{Fehling solution}]{2CuO} \underset{\text{red ppt.}}{Cu_2O\downarrow} + CH_3CH_2—COOH$



$\underset{\text{Propan-2-ol}}{CH_3—\underset{OH}{\underset{|}{C}H}—CH_3} \xrightarrow[\Delta,\ 300°C]{Cu} CH_3—CO—CH_3$

$\xrightarrow[\text{Fehling solution}]{2CuO} \text{No reaction}$

69. (*a*) The IUPAC name of $C_6H_5—O—C_2H_5$ is ethoxy benzene.

70. (*b*) **Lucas test:** In this test, the alcohol is treated with Lucas reagent which is an equimolar mixture of HCl and $ZnCl_2$. Alcohols are soluble in Lucas reagent and form a clear solution. On reaction, alkyl chlorides are formed which being insoluble result in turbidity in the solution.

$\text{Alcohol} \xrightarrow[ZnCl_2]{\text{conc. HCl}} \text{Alkyl chloride} + H_2O$

If turbidity appears immediately, tertiary alcohol is indicated.

If turbidity appears within five minutes, secondary alcohol is indicated.

If turbidity appears only upon heating, primary alcohol is indicated.

71. (*b*) For a compound to be optically active, it should contain at least one chiral centre.

butan-1ol does not contain any chiral carbon. Hence, it is optically inactive.

butan-2-ol contain one chiral carbon. Hence, it is optically active.

propan-1-ol does not contain any chiral carbon. Hence, it is optically inactive.

propan-2-ol does not contain any chiral carbon. Hence, it is optically inactive.

72. (*a*) **Lucas test:** In this test, the alcohol is treated with Lucas reagent which is an equimolar mixture of conc. HCl and $ZnCl_2$. Alcohols are soluble in Lucas reagent and form a clear solution. On reaction, alkyl chlorides are formed which being insoluble result in turbidity in the solution.

$\text{Alcohol} \xrightarrow[ZnCl_2]{\text{conc. HCl}} \text{Alkyl chloride} + H_2O$

If turbidity appears immediately, tertiary alcohol is indicated.

If turbidity appears within five minutes, secondary alcohol is indicated.

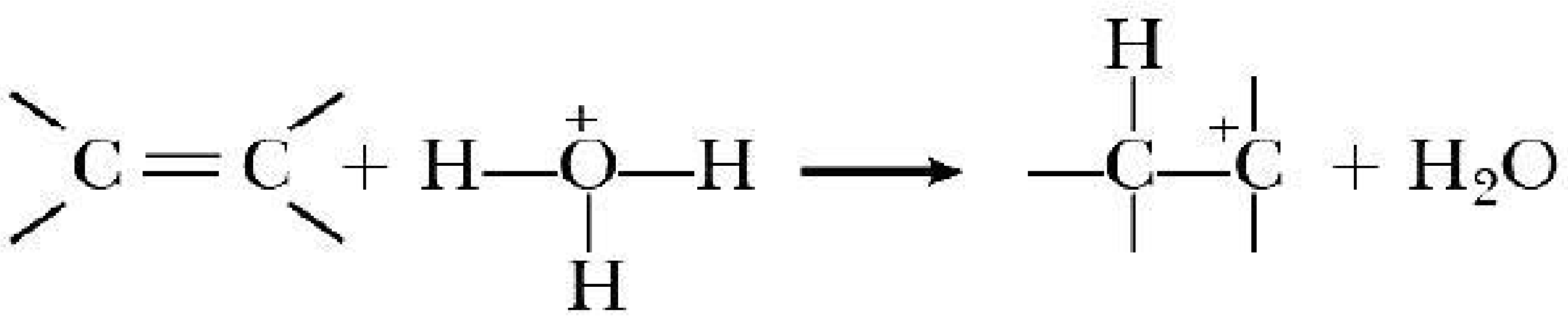
If turbidity appears only upon heating, primary alcohol is indicated.

73. (*b*) One per cent solution of phenol is used as a disinfectant and 0.2 per cent solution of phenol is an antiseptic so a higher concentration of the same compound is harmful to the body but can be used as a disinfectant to kill microorganisms on the non-living thing.

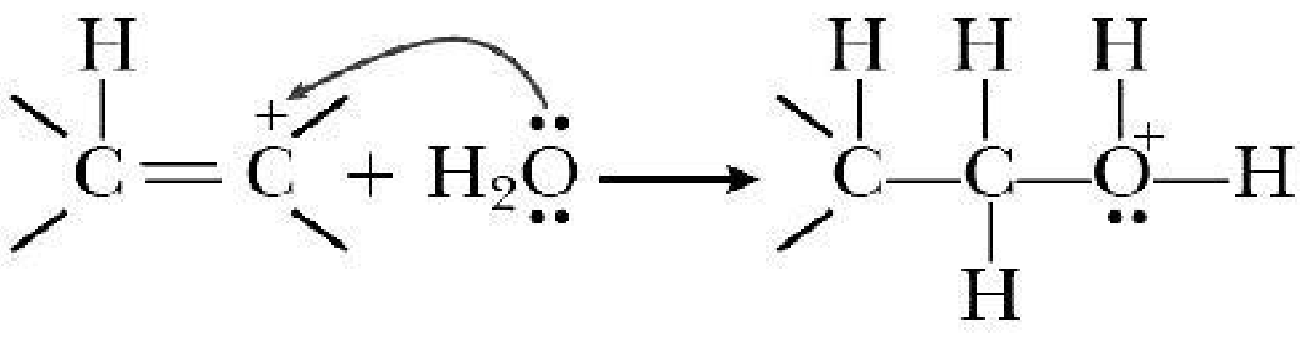
74. (*d*) There are three steps in the mechanism of acid catalysed hydration af an alkene to form corresponding alcohol.

Step 1 : Carbocation formation and carbocation is formed by attack of H_3O^+.

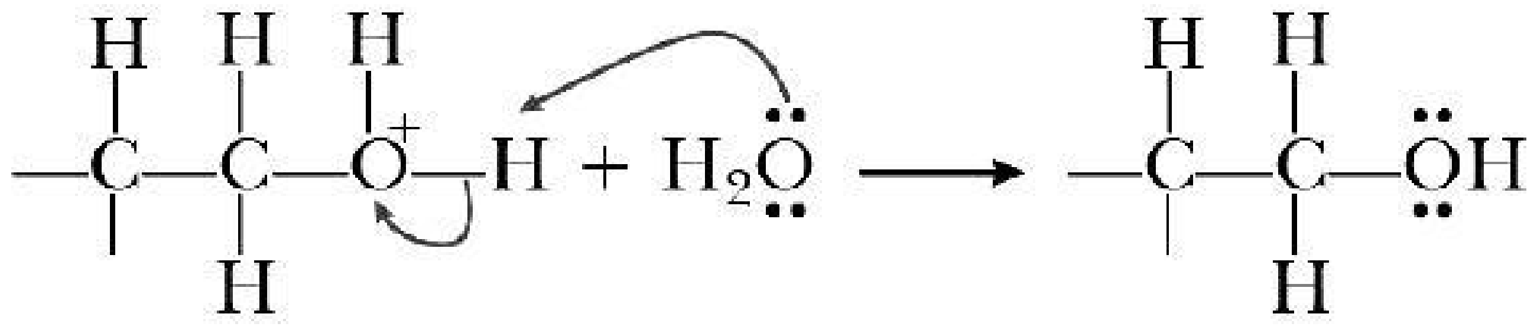
$$H_2O + \underset{\substack{\text{(From}\\ \text{an acid)}}}{H^+} \longrightarrow H_3O^+$$



Step 2 : Nucleophile H_2O attacks on carbocation.



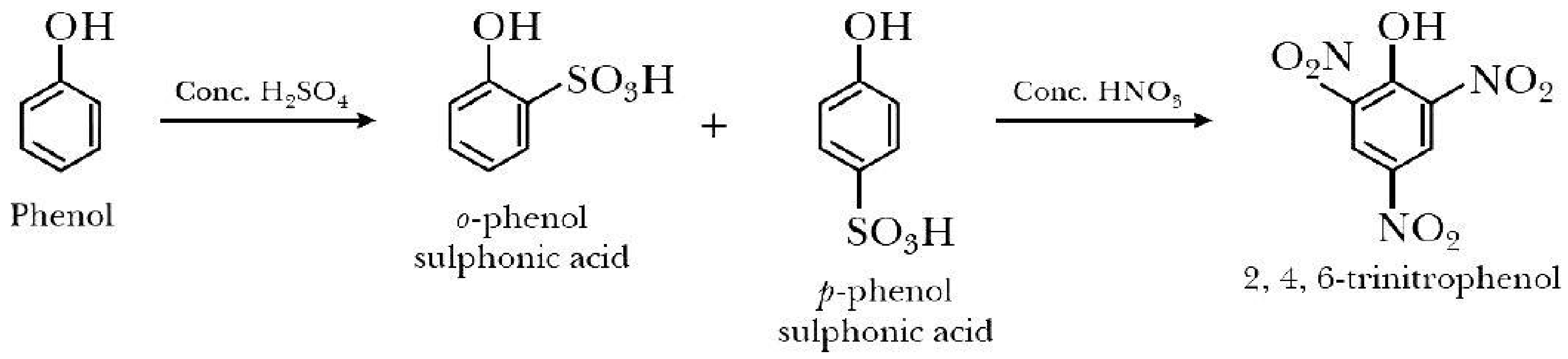
Step 3 : Deprotonation to form an alcohol.



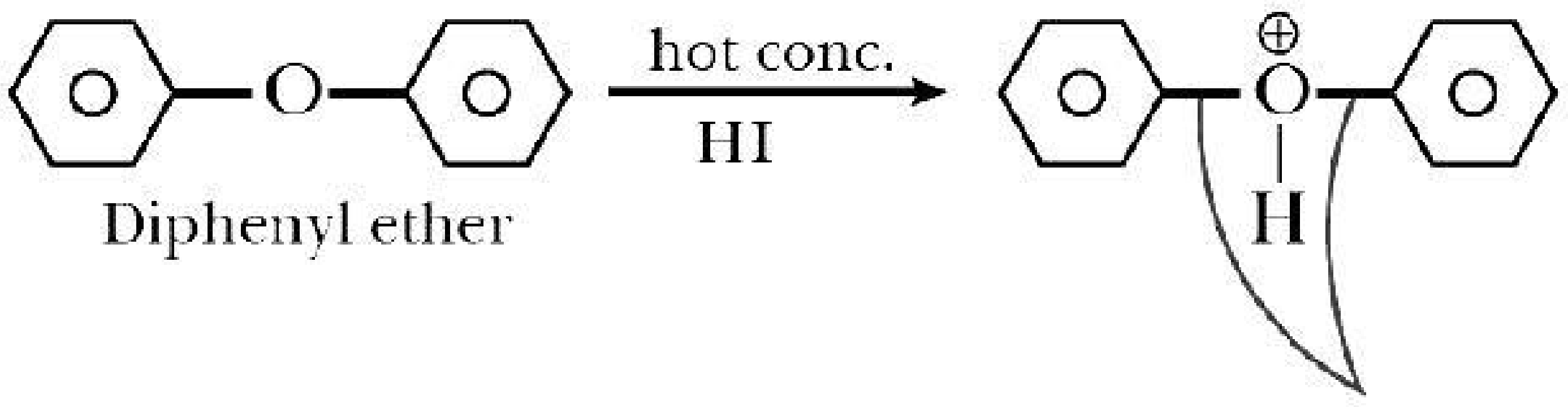
75. (*a*) A reagent named as pyridium chlorochromate (PCC) will carry out this reaction and its the most suitable reagent which can convert primary alcohol into aldehyde.PCC is a milder version of chromic acid. Essentially, what it does is oxidize alcohols one rung up the oxidation ladder, from primary alcohols to aldehydes and from secondary alcohols to ketones. Unlike chromic acid, PCC will not oxidize aldehydes to carboxylic acids.

76. (*c*) *m*-Methoxy phenol is the strongest acid. Methoxy group at meta position exerts only-I effect. Due to this, it withdraws electrons from all the nuclear position of the benzene ring including the one holding the —OH group. Consequently, electron density on the O—H bond decreases. Hence, *m*-methoxy phenol becomes more acidic than *o* and *p*-methoxy phenols.

77. (*b*)



78. (*d*)



Not break this bond due to double bond character because of resonance between the lone pair of electrons on the O atom and the C atom of the aryl group.

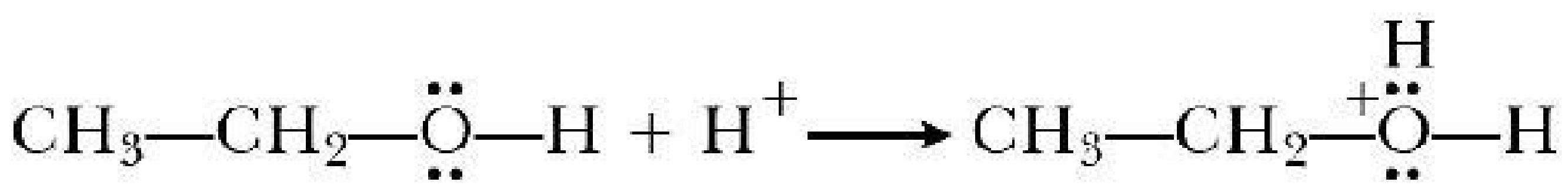
79. (*c*) **Williamson Ether Synthesis:**

80. (*a*) Ethanol is converted into ethoxy ethane by heating excess of ethanol with conc. sulphuric acid at 140°C.

Mechanism:

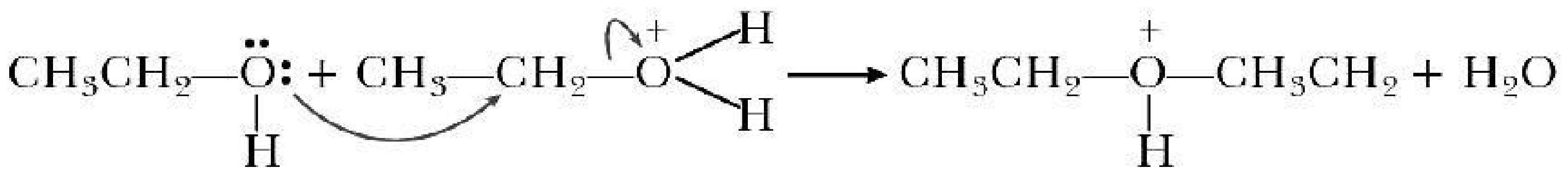
Formation of ether follows S_N2 mechanism.

Step 1



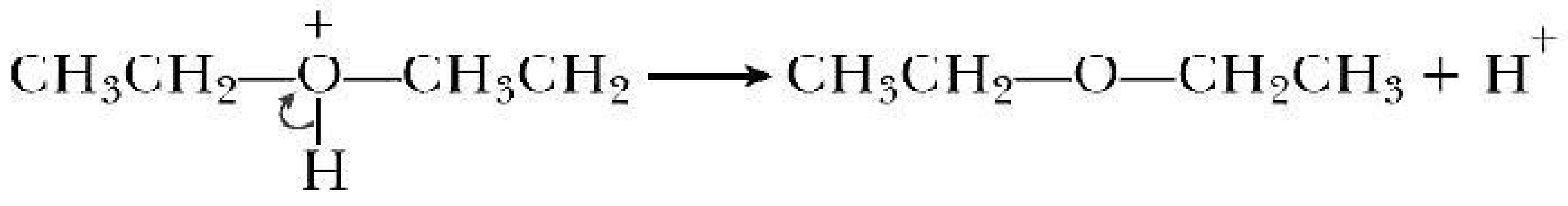
$$CH_3-CH_2-\underset{\cdot\cdot}{\ddot{O}}-H + H^+ \longrightarrow CH_3-CH_2-\overset{H}{\overset{+}{\underset{\cdot\cdot}{\ddot{O}}}}-H$$

Step 2



$$CH_3CH_2-\underset{H}{\underset{|}{\ddot{O}}}: + CH_3-CH_2-\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix} \longrightarrow CH_3CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_3CH_2 + H_2O$$

Step 3



$$CH_3CH_2-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_3CH_2 \longrightarrow CH_3CH_2-O-CH_2CH_3 + H^+$$

81. (*b*) $\underset{\text{Isopropyl methyl ether}}{(CH_3)_2CH-O-CH_3} + HI \longrightarrow \underset{\text{Isopropyl alcohol}}{(CH_3)_2CH-OH} + \underset{\text{Methyl iodide}}{CH_3I}$

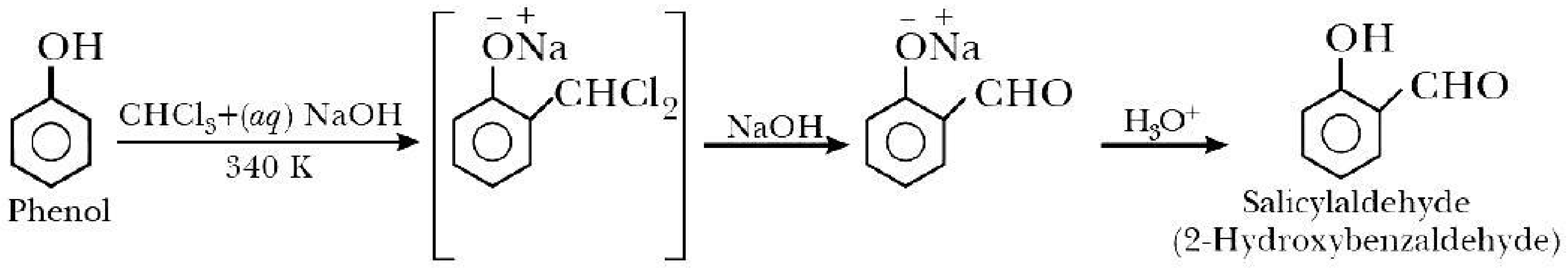
Here, iodine will attach to methyl forming methyl iodide.

82. (*d*) Primary alcohol or secondary alcohol(2-hydroxy propane) can be oxidized to the corresponding aldehyde, ketones or carboxylic acids by oxidation.

2-hydroxy propane vapour is provided moderately over the Ag dust at 250°C in presence of air to form carbonyl compound.

$$\underset{2^\circ\text{ alcohol}}{CH_3-CH(OH)-CH_3} \xrightarrow{O_2,\text{ Ag dust}} \underset{\text{Ketone}}{CH_3COCH_3} + H_2O$$

83. (*a*) **Reimer–Tiemann reaction:** Treatment of phenol with chloroform in the presence of sodium hydroxide followed by hydrolysis of resulting product gives *o*-hydroxybenzaldehyde (salicylaldehyde) as a major product.



Note: $OH^- + CHCl_3 \rightleftharpoons CCl_3^- + H_2O \longrightarrow \underset{\substack{\text{Dichlorocorbene}\\\text{(Electrophile)}}}{:CCl_2} + Cl^-$

84. (*d*) Deprotonation of *p*-nitrophenol gives *p*-nitrophenoxide ion. The negative charge on O atom is stabilised as strongly electron withdrawing nitro group is present at para position (—R effect). This effect is some what less in *m*-nitrophenol as at *m*-position, —NO_2 groups withdraws electron by weaker —I effect. In case of *p*-aminophenol, deprotonation gives *p*-aminophenoxide ion. The negative charge on O atom is destabilised as electron releasing amino group is present in para position. Therefore, *p*-nitrophenol is most acidic.

85. (*a*)

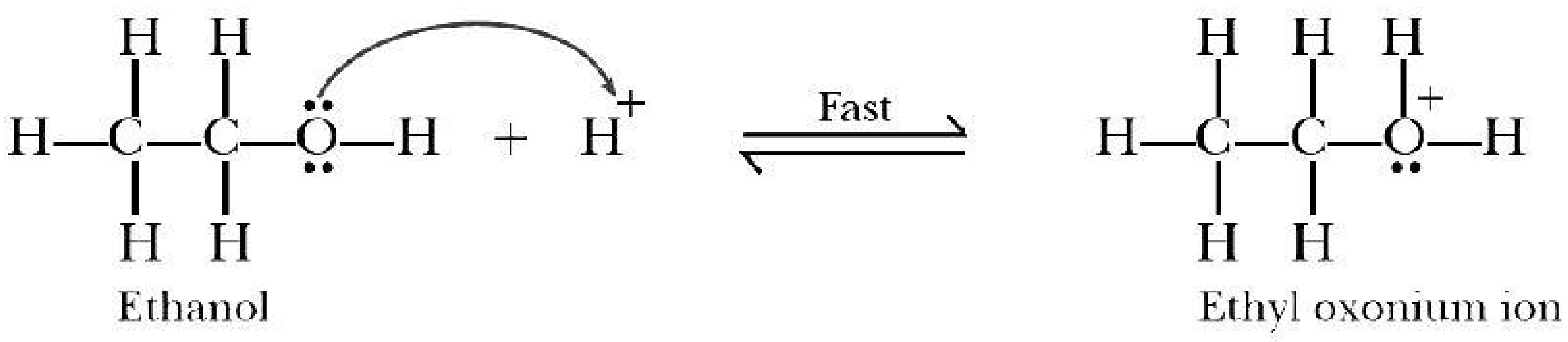
$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PCl_5} \underset{\substack{\text{Ethyl chloride}\\(B)}}{CH_3CH_2Cl} \xrightarrow{\text{Alc. KOH}} \underset{\substack{\text{Ethene}\\(C)}}{CH_2{=}CH_2}$$

86. (*a*) The given reaction is known as Williamson's synthesis. In general, it is written as

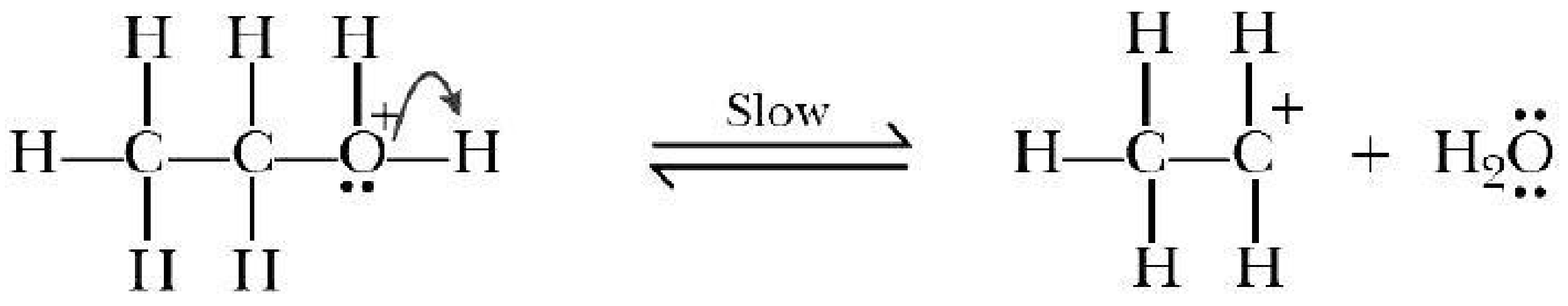
$$R{-}X + \overset{+}{Na}{-}\overset{-}{O}{-}R' \longrightarrow R{-}O{-}R' + NaX$$

87. (*d*) The mechanism of dehydration of ethanol involves the following steps:

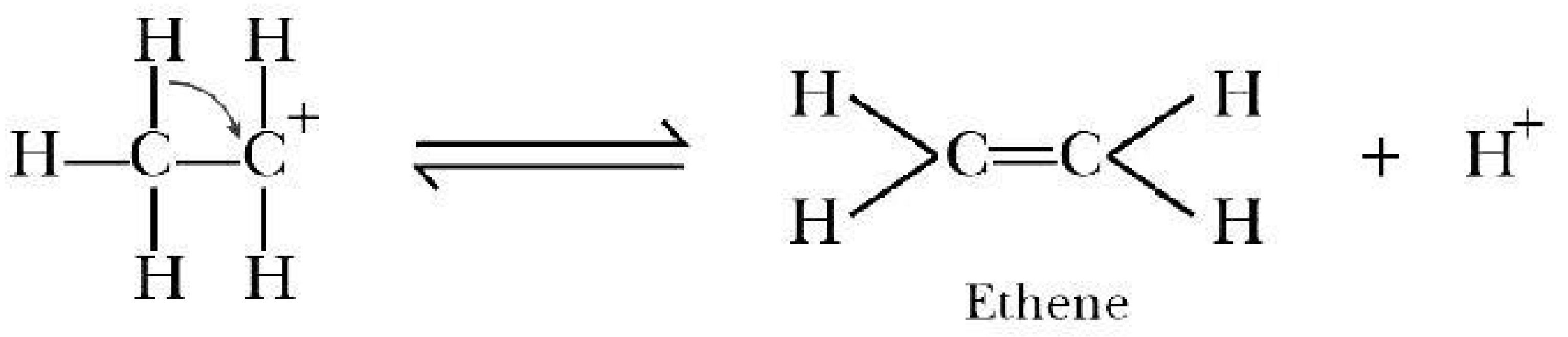
Step 1: Formation of protonated alcohol



Step 2: Formation of carbocation: It is the slowest step and hence, the rate determining step of the reaction.



Step 3: Formation of ethane by elimination of a proton



The acid used in step 1 is released in step 3. To drive the equilibrium to the right, ethene is removed as it is formed.

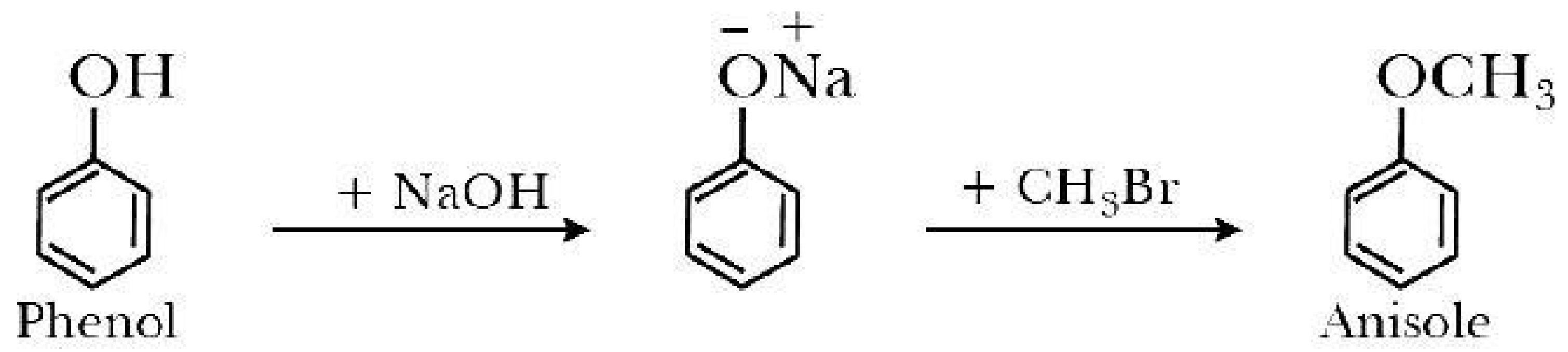
88. (*d*) Cobalt naphthenate is the catalyst used in a commercial method of preparation of phenol. Alkaline solution of cumene(isopropyl benzene) in sodium carbonate is oxidised with air/oxygen in presence of cobalt naphthenate catalyst to form cumene hydroperoxide. Cumene hydroperoxide on heating with dilute H_2SO_4 decomposes to give phenol and acetone.

89. (*c*) Nitro group has both $-R$ effect and $-I$ effect, but $-R$ effect predominates. Due to stronger electron withdrawing nature of $-NO_2$ group, phenoxide ion is stabilized more. Hence nitrophenol is more acidic than phenol. Methyl group destabilizes the phenoxide ion by $+I$ effect and hyper conjugation. Hence *m*-cresol is weaker acid than phenol. Chlorine have both $+R$ and $-I$ effect, but $-I$ effect predominates. Hence *o*-chlorophenol is more acidic than phenol. $-R$ effect of nitro group is stronger than $-I$ effect of chlorine, hence *m*-nitrophenol is more acidic than *o*-chlorophenol. Therefore the correct order of acidic strength is

m-nitrophenol > *o*-chlorophenol > phenol > *m*-cresol

Acidic strength in increasing order is *ii* < *iii* < *iv* < *i*

90. (*b*)



91. (*c*) The reaction between$(CH_3)_3COCH_3$ and HI follows S_N1 mechanism. For an S_N1 reaction, the formation of product is controlled by stability of the carbocation formed in the slowest step. Since tert.butyl carbonium ion$(CH_3)_3\overset{\oplus}{C}$ formed after the cleavage of C—O bond in the slowest step is more stable than methyl carbonium ion$(\overset{\oplus}{C}H_3)$ therefore$(CH_3)_3C{-}I$ and CH_3OH are the main products.

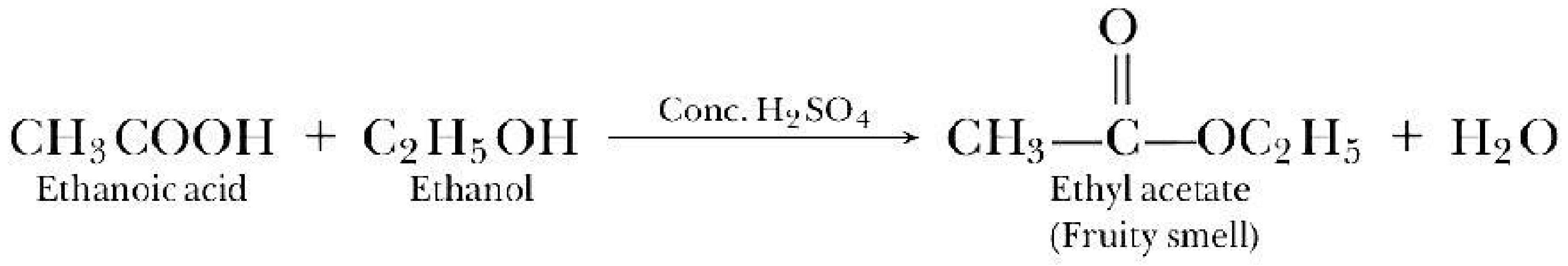
92. (*d*) **Iodoform test:** When ethyl alcohol or any alcohol containing the group $CH_3-\overset{\overset{OH}{|}}{C}H-$ or $CH_3-\overset{\overset{O}{\|}}{C}-$ group is heated with iodine and aqueous NaOH or Na_2CO_3 solution at 333–343 K, a yellow precipitate of iodoform is obtained.

Among the given compounds, isobutyl alcohol $(CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-OH)$ does not contain $CH_3-\underset{\underset{OH}{|}}{C}H-$ group and hence, does not undergo iodoform reaction.

93. (*a*) Propan-1-ol has the possibility of the formation of hydrogen bonds. Intermolecular hydrogen bonds formation takes place in propan-1-ol because of highly electronegative oxygen atom. Hence it has highest Boiling point.

94. (*c*) A liquid + $C_2H_5OH \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{(Fruity smell)}}{\text{Compound}}$

Fruity smell is the characteristic property of an ester. Thus, the above reaction leads to the formation of an ester.

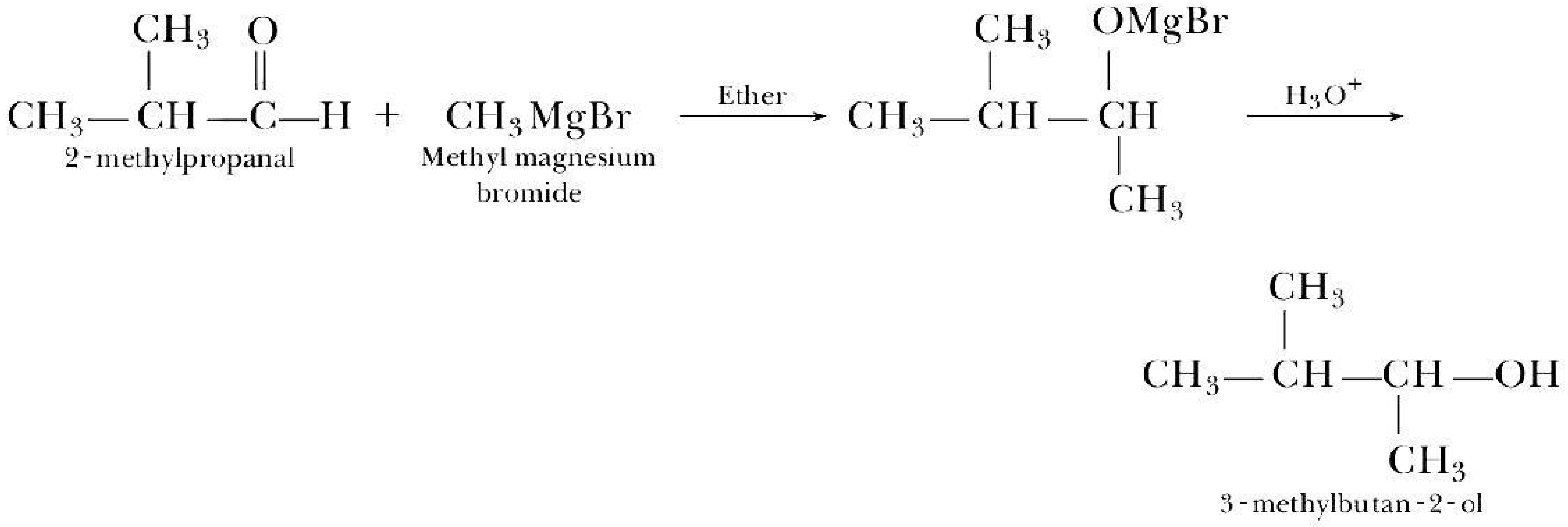


$$\underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\substack{\text{Ethyl acetate}\\ \text{(Fruity smell)}}}{CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} + H_2O$$

The reaction is called as esterification

95. (*b*) Formation of a yellow precipitate on heating a compound with an alkaline solution of iodine is known as iodoform reaction. Methyl alcohol does not respond to this test. Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketones and those alcohols which possess $CH_3CH(OH)$ - group.

96. (*d*)



$$\underset{\text{2-methylpropanal}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-\overset{\overset{O}{\|}}{C}-H} + \underset{\substack{\text{Methyl magnesium}\\ \text{bromide}}}{CH_3MgBr} \xrightarrow{\text{Ether}} CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{CH_3}{|}}{\overset{\overset{OMgBr}{|}}{C}H} \xrightarrow{H_3O^+}$$

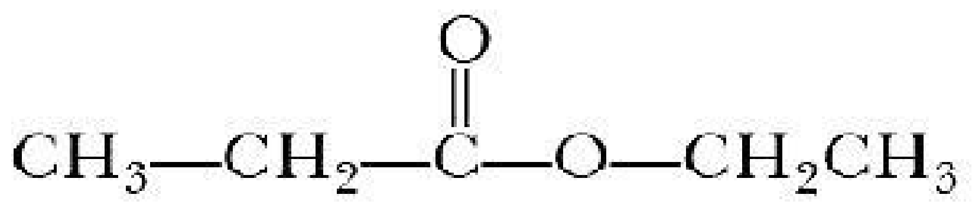
$$\underset{\text{3-methylbutan-2-ol}}{CH_3-\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{CH_3}{|}}{C}H-OH}$$

97. (*c*) Ethers are the compounds with general formula of $C_nH_{2n+2}O$ (same as monohydric alcohols). These are represented by general structure, R—O—R′.

98. (*b*) Phenyl magnesium bromide reacts with tert-butanol to produce benzene because phenyl is an electronegative group which is associated with active hydrogen of alcohol *i.e.* —H of —OH group of alcohol.

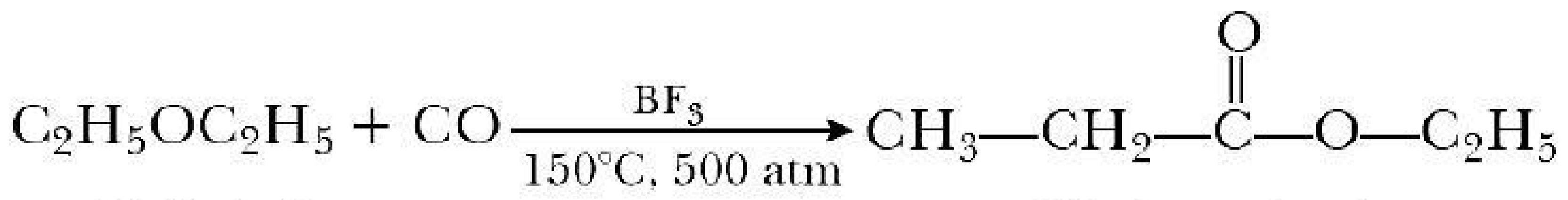
$$C_6H_5\boxed{MgBr + (CH_3)_3C-O}H \longrightarrow \underset{\text{benzene}}{C_6H_6} + (CH_3)_3C-O-MgBr$$

99. (*c*) Structure of ethyl propionate—



$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2CH_3$$

Preparation of ethyl propionate—



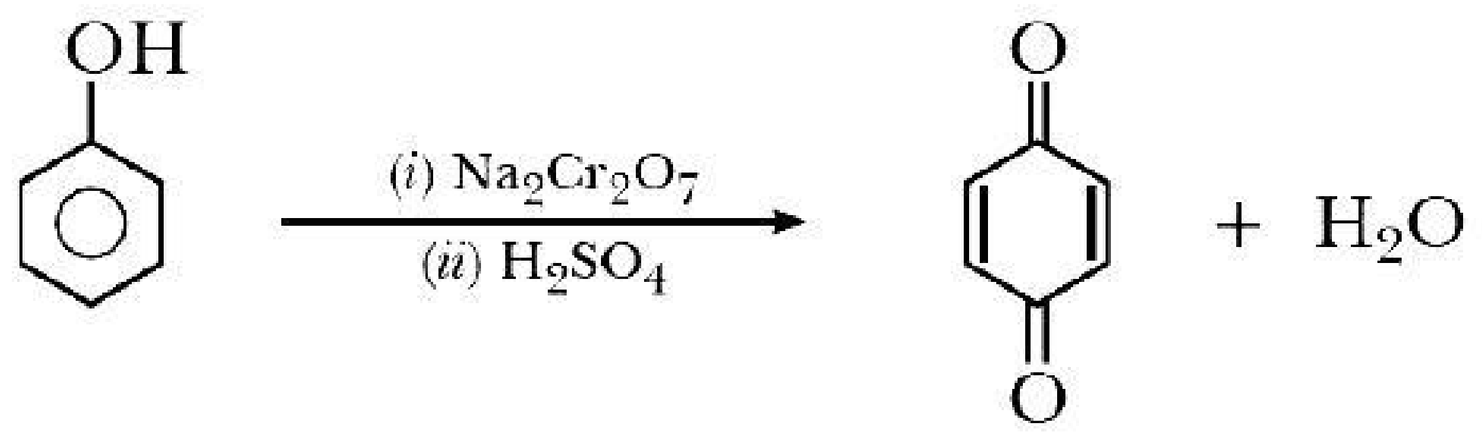
$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + CO \xrightarrow[150°C,\ 500\ atm]{BF_3} \underset{\text{Ethyl propionate}}{CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-O-C_2H_5}$$

Diethyl ether

Ethyl propionate

100. (*d*) Ethanol is converted to ethylene by using conc. H_2SO_4 at 170°C. Conc. H_2SO_4 at 170°C acts as a dehydrating reagent and due to dehydration of ethanol it is converted into ethylene and water.

101. (*b*)



Benzoquinone

102. (*a*) **Lucas test:** In this test, the alcohol is treated with Lucas reagent which is an equimolar mixture of conc. HCl and $ZnCl_2$. Alcohols are soluble in Lucas reagent and form a clear solution. On reaction, alkyl chlorides are formed which being insoluble result in turbidity in the solution.

$$\text{Alcohol} \xrightarrow[ZnCl_2]{\text{conc. HCl}} \text{Alkyl chloride} + H_2O$$

If turbidity appears immediately, tertiary alcohol is indicated.

If turbidity appears within five minutes, secondary alcohol is indicated.

If turbidity appears only upon heating, primary alcohol is indicated.

103. (*d*) Ethanol is distilled with bleaching powder to form chloroform.

The reactions involved are as follows:

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

$$CH_3CH_2OH + [O] \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHO + 3Cl_2 \longrightarrow Cl_3CHO + 3HCl$$

Chlorine is an oxidising agent as well as chlorinating agent.

$$2CCl_3CHO + Ca(OH)_2 \xrightarrow{\text{hydrolysis}} 2CHCl_3 + (HCOO)_2Ca$$

Hence, $CaOCl_2$ and H_2O reacts with ethanol to form chloroform.

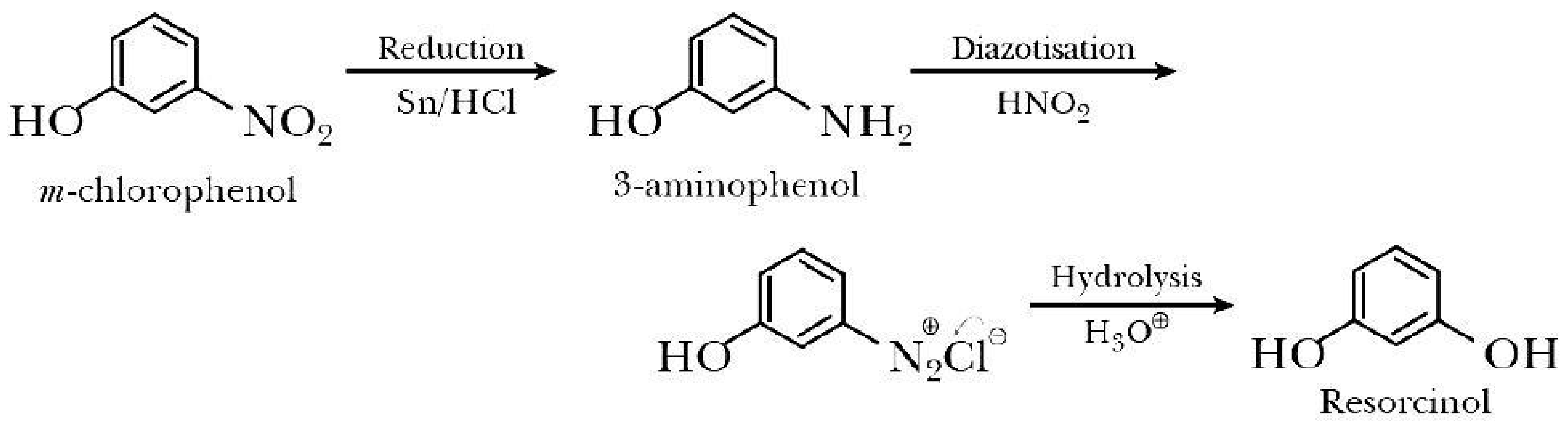
104. (*a*) Neutral $FeCl_3$ forms violet coloured complex with phenol whereas it forms buff coloured precipitate of ferric benzoate with benzoic acid.

105. (*d*) An alcohol such as ethylalcohol(C_2H_5OH) converts methyl magnesium iodide to methane in one step.

$$C_2H_5OH + CH_3MgI \longrightarrow CH_4 + Mg(OC_2H_5)I$$

106. (*a*) *o*-, *m*- and *p*- cresol, all contains phenolic group, thus they give violet colouration with $FeCl_3$ whereas benzyl alcohol and methyl phenyl ether do not contain phenolic group, hence give no colouration with $FeCl_3$. Hence the pair of compounds which are identifiable by $FeCl_3$ is o-cresol and benzyl alcohol.

107. (*c*)



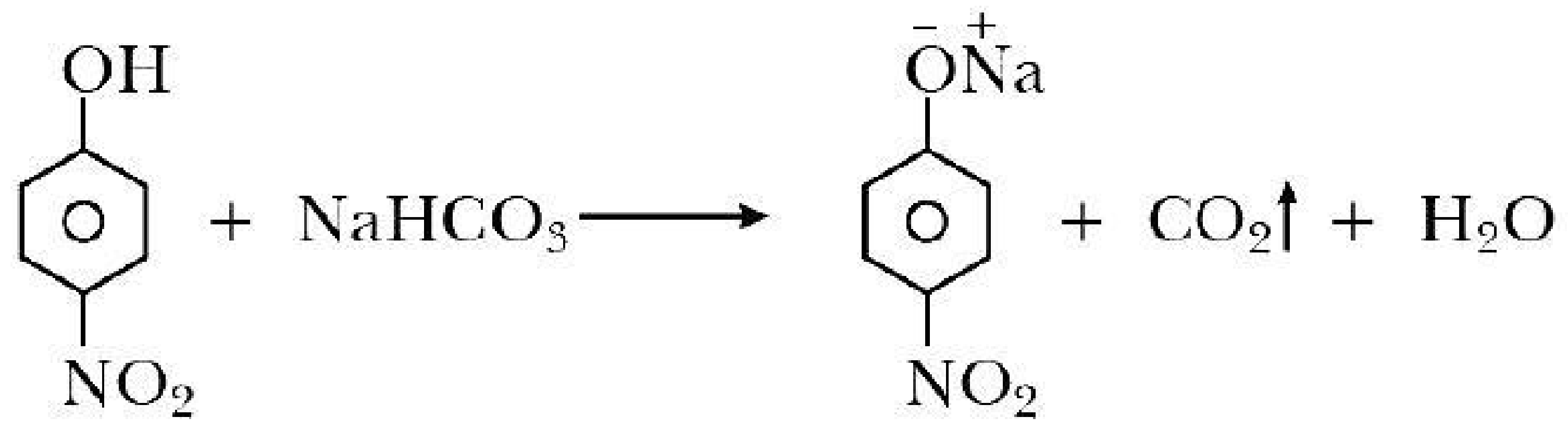
108. (*d*) An ether is more volatile than an alcohol having the same molecular formula. This is due to intermolecular hydrogen bonding in alcohols. In alcohols, H atom is attached to strongly electronegative O atom. Therefore, they exist as an associated molecule due to hydrogen bonding.

109. (*b*) Starch $\xrightarrow{\text{Diastase}}$ Maltose $\xrightarrow{\text{Maltase}}$ Glucose $\xrightarrow{\text{Zymase}}$ Ethanol

110. (*d*) The balanced chemical equation for the reaction of benzene sulphonic acid with sodium bicarbonate is

$$C_6H_5SO_3H + NaHCO_3 \longrightarrow C_6H_5SO_3^-Na^+ + CO_2\uparrow + H_2O$$

The balanced chemical equation for the reaction of *p*-nitrophenol with $NaHCO_3$ is



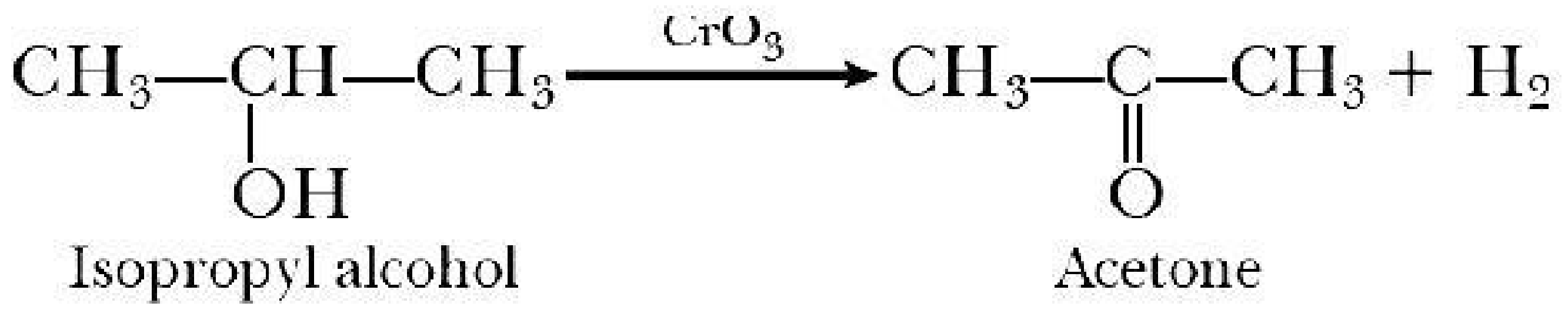
111. (*a*) $\underset{\substack{\text{Ethanol}\\(X)}}{C_2H_5OH} + K_2Cr_2O_7 \xrightarrow{H_2SO_4} \underset{\substack{\text{Ethanoic acid}\\(Y)}}{CH_3COOH}$

$$CH_3COOH + LiAlH_4 \xrightarrow{H^+} \underset{\substack{\text{Ethanol}\\(X)}}{CH_3CH_2OH}$$

112. (*c*) *n*-propyl alcohol oxidize with acidified $K_2Cr_2O_7$ to give propanoic acid while isopropyl alcohol oxidizes with acidified $K_2Cr_2O_7$ to give propanone.

113. (*c*) $R—CH_2—CH_2OH \xrightarrow{PBr_3} R—CH_2—CH_2—Br \xrightarrow{KCN} R—CH_2—CH_2CN \xrightarrow{H_3O^+} RCH_2CH_2COOH$

114. (*b*) On catalytic dehydrogenation, primary alcohols give aldehydes, secondary alcohols give ketones and tertiary alcohols give an alkene.



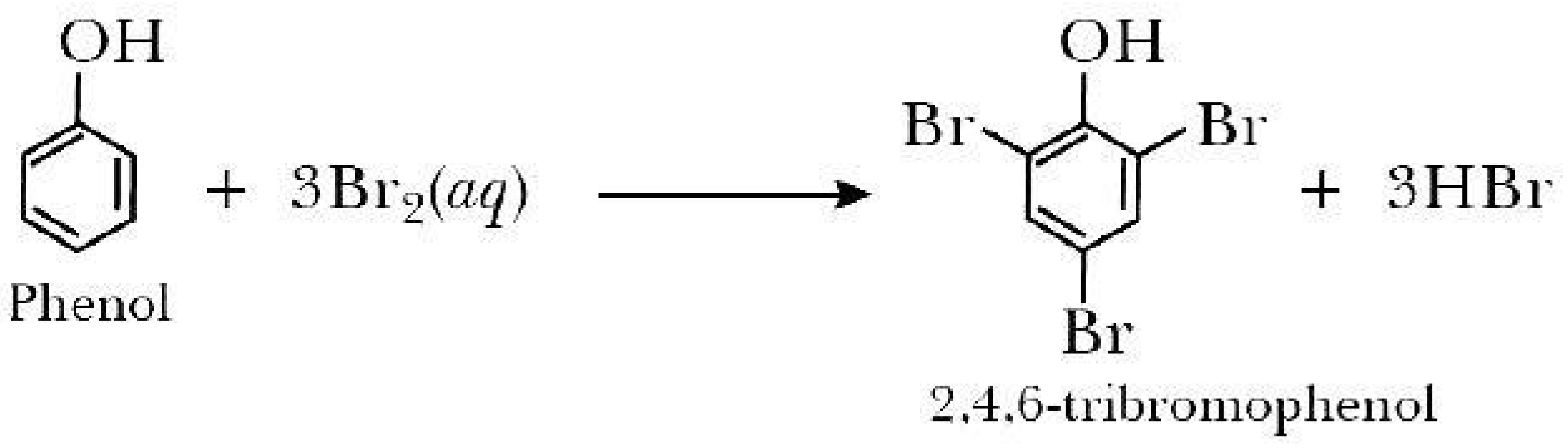
$$\underset{\text{Isopropyl alcohol}}{CH_3—\underset{\substack{|\\OH}}{C}H—CH_3} \xrightarrow{CrO_3} \underset{\text{Acetone}}{CH_3—\underset{\substack{\|\\O}}{C}—CH_3} + H_2$$

115. (*b*) The best method to prepare cyclohexene from cyclohexanol is by conc. H_3PO_4 because in given options dehydrating agent is conc. H_3PO_4.

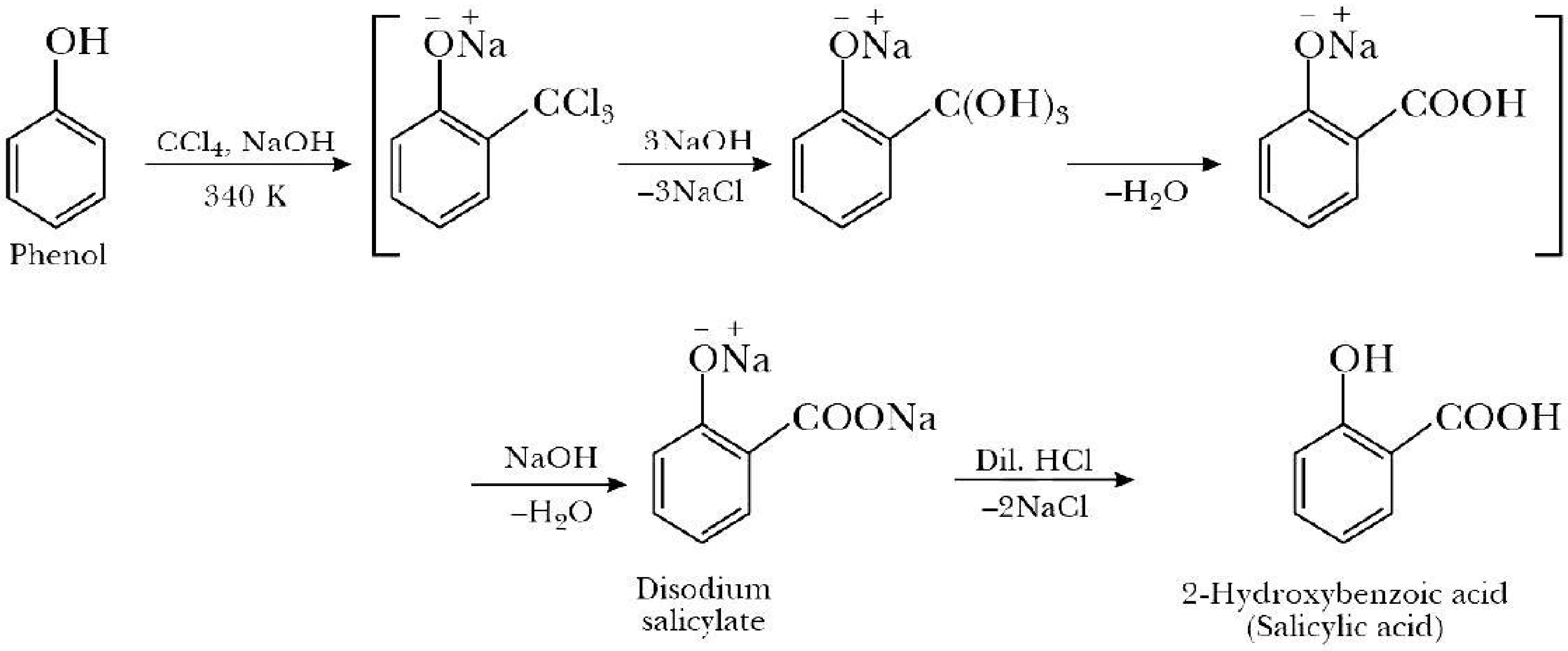
116. (*a*) Br_2 is formed by a redox reaction.

$$5Br^- + BrO_3^- + 6H^+ \longrightarrow 3Br_2 + 3H_2O$$

–OH group is the activating group and thus activates the benzene towards electrophilic substitution reaction at *o* and *p*-positions giving yellowish white precipitate of 2,4,6-tribromophenol.



117. (*a*)



119. (*d*) In $CH_3—CH_2—OH$, the electronegativity order is $H < C < O$

Since the most electronegativity difference is between O and H. Therefore, the bond will have more ionic character and can be break easily. Thus, O—H bond will undergo heterolytic cleavage readily.

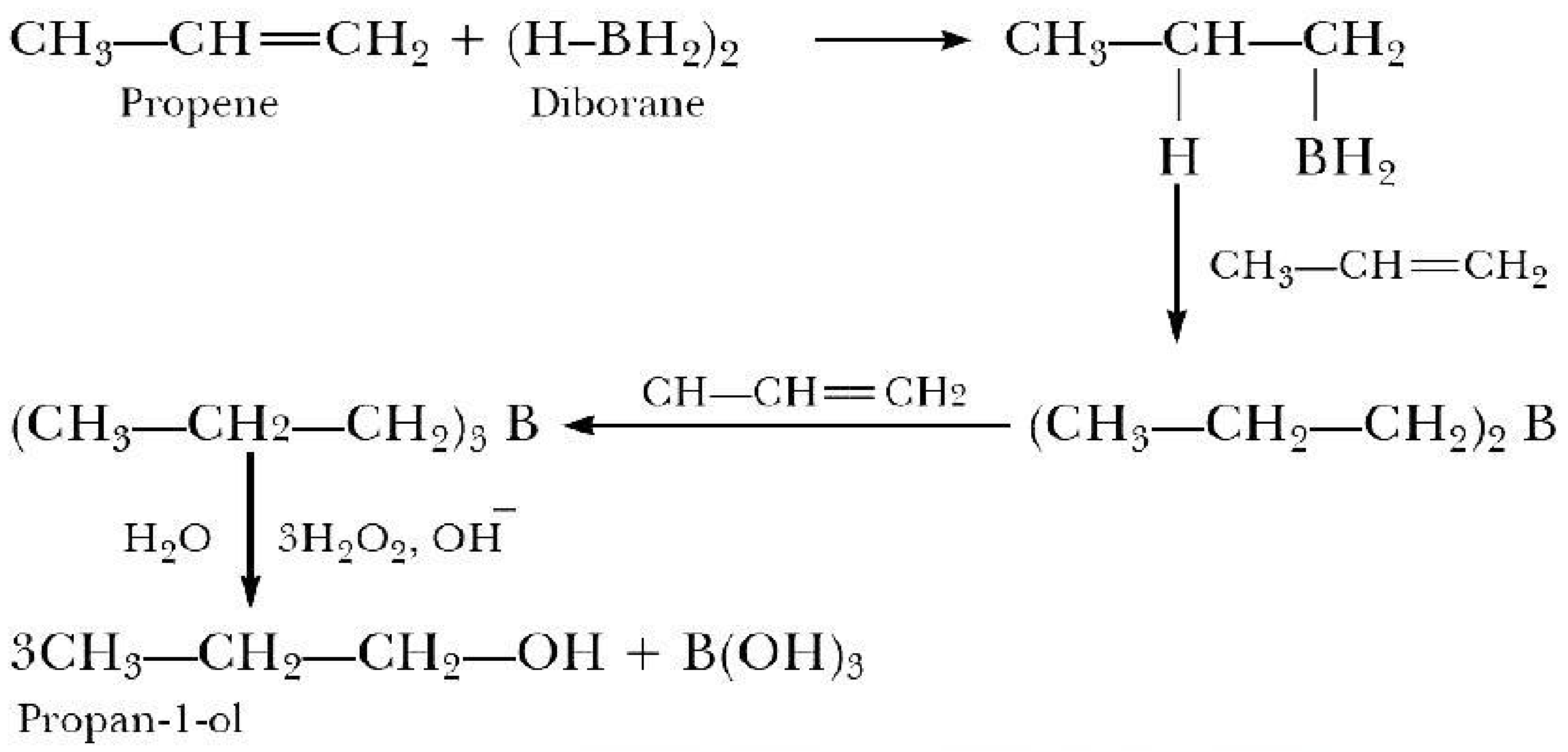
120. (*d*) Since the secondary alcohol on oxidation gives two different acids containing lesser number of carbon atom than the original alcohol. Thus, the alcohol is secondary alcohol and will contain 5 C atoms as it is forming acetic acid and propanoic acid.

121. (*d*) $\underset{\substack{\text{Glucose}\\\text{or}\\\text{Fructose}}}{C_6H_{12}O_6} \xrightarrow[\text{Yeast}]{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$

122. (*d*) $—OCH_3$, $—CH_3$ being electron donating groups decreases the acidic character of phenols. $—NO_2$, $—CN$ are electron withdrawing groups, tend to increase the acidic character. Moreover, $—OCH_3$ group is more electron donating than $—CH_3$ group.

Thus, the order is *p*-methoxphenol < *p*-methylphenol < *p*-nitrophenol.

123. (*b*) Propan-1-ol is produced by the hydroboration-oxidation reaction of propene. In this reaction, propene reacts with diborane $(BH_3)_2$ to form trialkyl borane as an addition product. This addition product is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

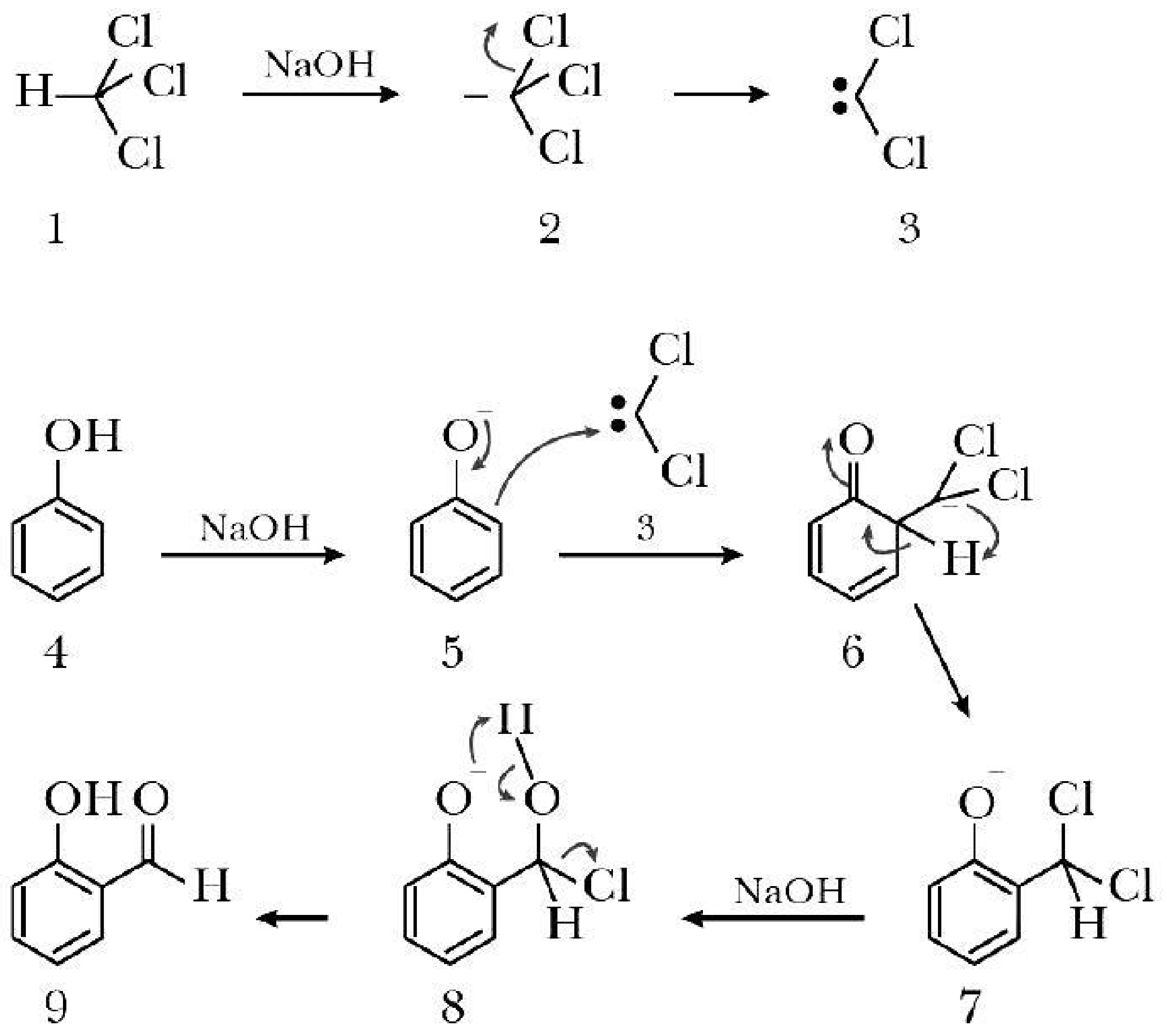


$$\underset{\text{Propene}}{CH_3—CH{=}CH_2} + \underset{\text{Diborane}}{(H–BH_2)_2} \longrightarrow CH_3—\underset{H}{\underset{|}{CH}}—\underset{BH_2}{\underset{|}{CH_2}} \xrightarrow{CH_3—CH{=}CH_2} (CH_3—CH_2—CH_2)_2\,B$$

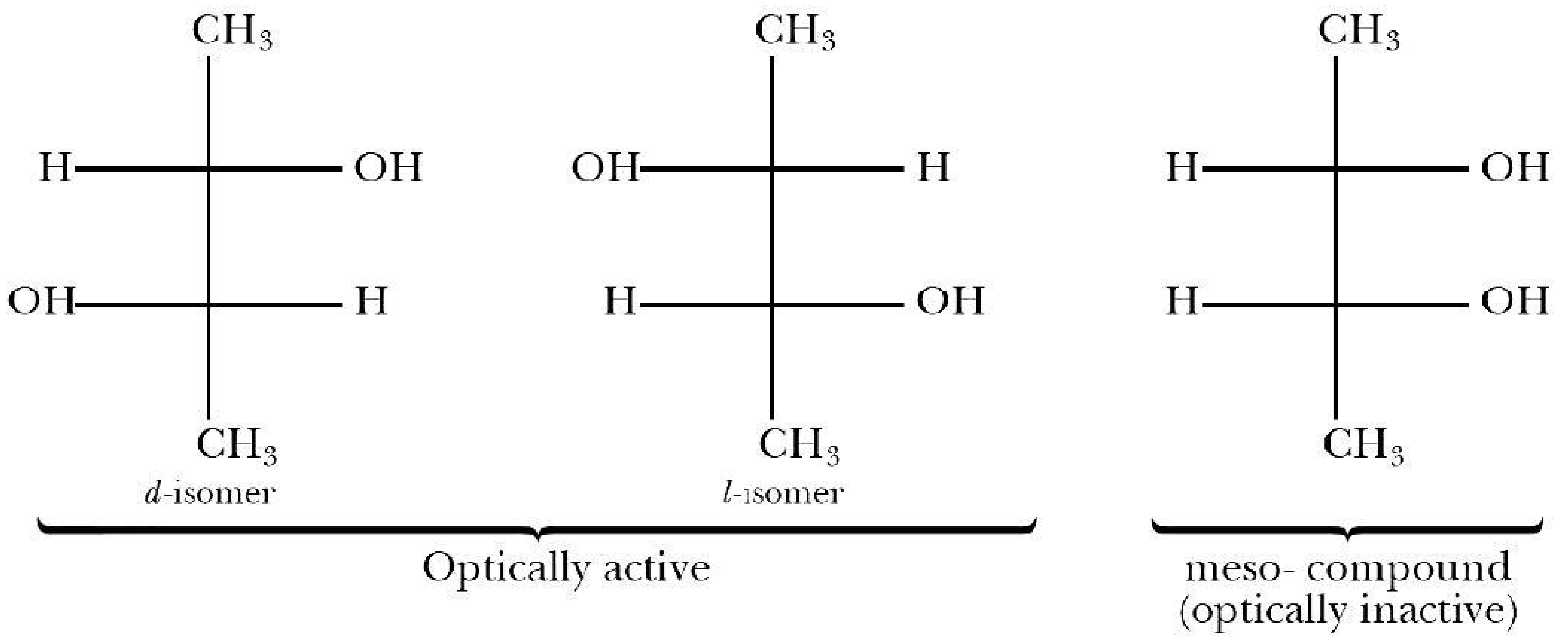
$$(CH_3—CH_2—CH_2)_2\,B \xrightarrow{CH—CH{=}CH_2} (CH_3—CH_2—CH_2)_3\,B \xrightarrow[H_2O]{3H_2O_2,\ \overline{O}H} \underset{\text{Propan-1-ol}}{3CH_3—CH_2—CH_2—OH} + B(OH)_3$$

124. (*a*) The presence of –OH groups in a compound leads to hydrogen-bonding which greatly increases its boiling point. Generally, the more 'exposed' the –OH group, the better it can participate in intermolecular H-bonding and thus, the boiling point will elevate. By that logic, primary alcohols will have the highest boiling point while tertiary alcohols will have the lowest boiling point.

125. (*b*) In the given reaction, the electrophile involved is dichlorocarbene(:CCl_2). In Reimer-Tiemann reaction, phenol in presence of NaOH/KOH reacts with chloroform to give salicyladehyde.



126. (*b*) The number of optically active stereoisomers possible for butan-2, 3–diol is 2. They are *d* and *l* isomers which are optically active. The meso-compound is optically inactive due to internal compensation.



127. (*a*) The ether when treated with HI produces both benzyl iodide or phenol.