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Alcohols,Phenols and Ethers

Alcohols

1.Introduction and Classifications
2.Nomenclature (IUPAC and Trivial)
3.Preparation of Alcohols : using Grignard Reagent, .Ester Hydrolysis, Reduction of Aldehydes , Ketones, Acids and Esters
4.Chemical Reactions: With Sodium, HX (Lucas Test), Esterification, Oxidation (with PCC, Alcoholic KMn04, Acidic Dichromate, Cone. HN03) ·
5.Oppenauer Oxidation, Oxidation of Diols, Pinacol-Pinacolone Rearrangement

Phenols

1.Introduction - Classifications

2.Nomenclature - (IUPAC and Trivial)

3.Preparation of Phenol:

Cumene

Hydro.peroxide Method

From Diazonium salts.

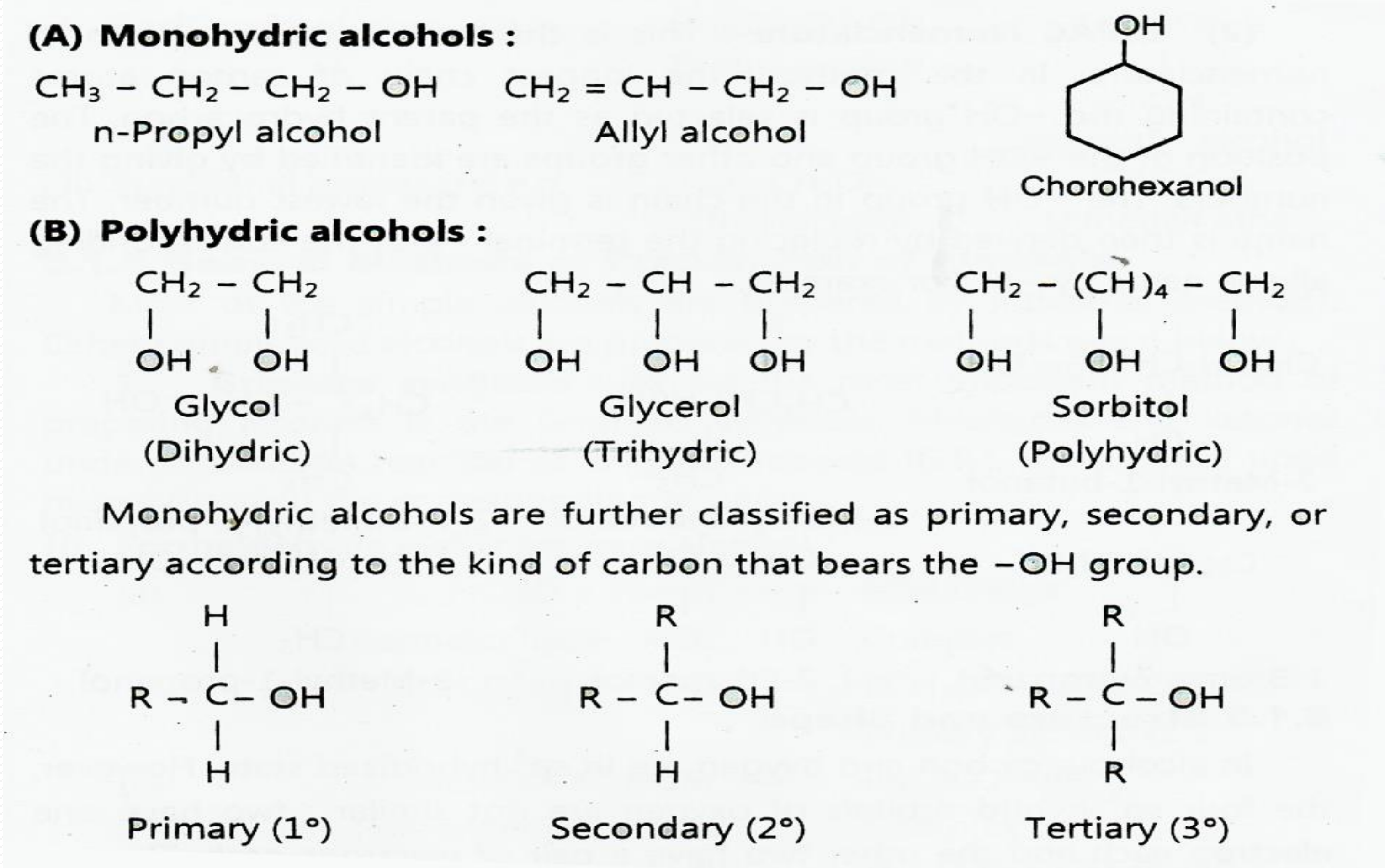
4.Comparison - Phenols and Alcohols

5.Chemical Reactions: Eledrophilic Substitution (Nitration, Halogenation and Sulphonat ion) Reimer-Tiemann Reaction, Gattermann·-Koch Reaction, Houben-Hoesch Condensation, Schotten-Baumann Reaction

Ethers

1. Introduction
2. Methods of Preparation
    I)Williamson’s
    II)Daizomethane
3. Reactions of Ethers

Classification



(A) Monohydric alcohols :

$CH_3 - CH_2 - CH_2 - OH$
n-Propyl alcohol

$CH_2 = CH - CH_2 - OH$
Allyl alcohol

OH

Chorohexanol

(B) Polyhydric alcohols :

$$\begin{array}{ccc} CH_2 & - & CH_2 \\ | & & | \\ OH & & OH \end{array}$$

Glycol
(Dihydric)

$$\begin{array}{ccccc} CH_2 & - & CH & - & CH_2 \\ | & & | & & | \\ OH & & OH & & OH \end{array}$$

Glycerol
(Trihydric)

$$\begin{array}{ccccc} CH_2 & - & (CH)_4 & - & CH_2 \\ | & & | & & | \\ OH & & OH & & OH \end{array}$$

Sorbitol
(Polyhydric)

Monohydric alcohols are further classified as primary, secondary, or tertiary according to the kind of carbon that bears the −OH group.

$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ R & - & C & - & OH \\ & & | & & \\ & & H & & \end{array}$$

Primary (1°)

$$\begin{array}{ccccc} & & R & & \\ & & | & & \\ R & - & C & - & OH \\ & & | & & \\ & & H & & \end{array}$$

Secondary (2°)

$$\begin{array}{ccccc} & & R & & \\ & & | & & \\ R & - & C & - & OH \\ & & | & & \\ & & R & & \end{array}$$

Tertiary (3°)

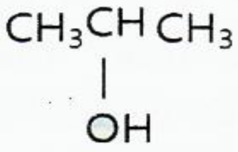
Nomenclature Of Alcohol

- *Alcohols are named by two ways :*

(1) Common or Trivial Name : The lower and simple alcohols are often named by the alkyl group followed by the word alcohol. For example,

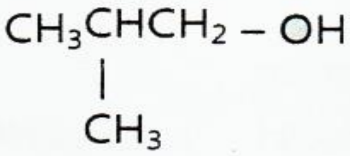
CH_3CH_2-OH

Ethyl alcohol



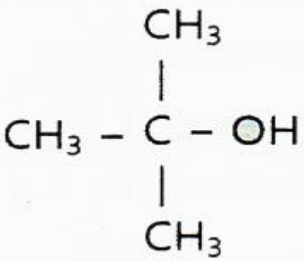
$CH_3\underset{\substack{|\\OH}}{CH}CH_3$

Iso-propyl alcohol



$CH_3\underset{\substack{|\\CH_3}}{CH}CH_2-OH$

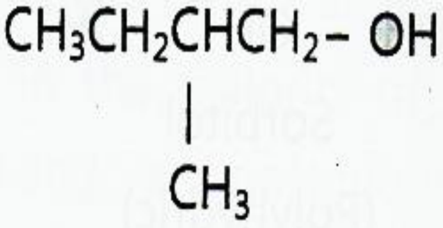
Iso-butyl alcohol



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

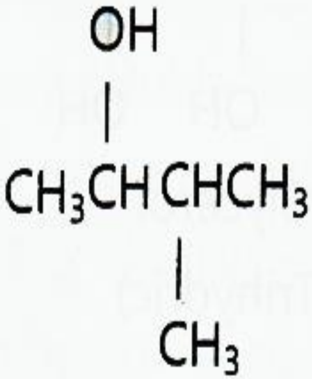
tertiary-Butyl alcohol

IUPAC Nomenclature of Alcohols



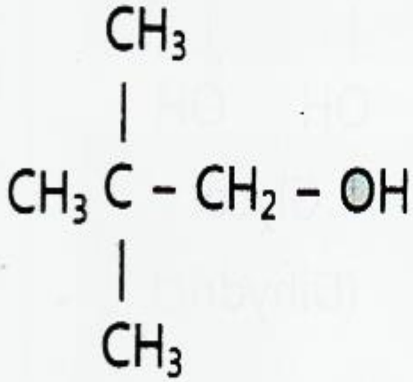
$$\mathrm{CH_3CH_2\underset{\underset{CH_3}{|}}{C}HCH_2-OH}$$

2-Methyl-1-butanol



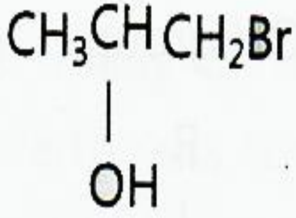
$$\mathrm{CH_3\overset{\overset{OH}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_3}$$

3-Methyl-2-butanol



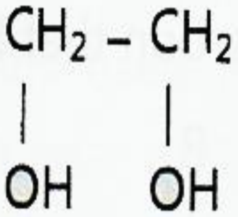
$$\mathrm{CH_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-OH}$$

2, 2-Dimethyl-1-propanol



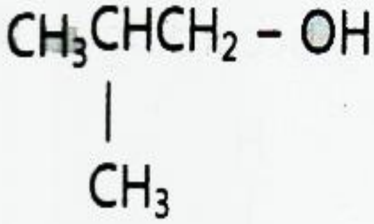
$$\mathrm{CH_3\underset{\underset{OH}{|}}{C}H\,CH_2Br}$$

1-Bromo-2-propanol



$$\mathrm{\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}}$$

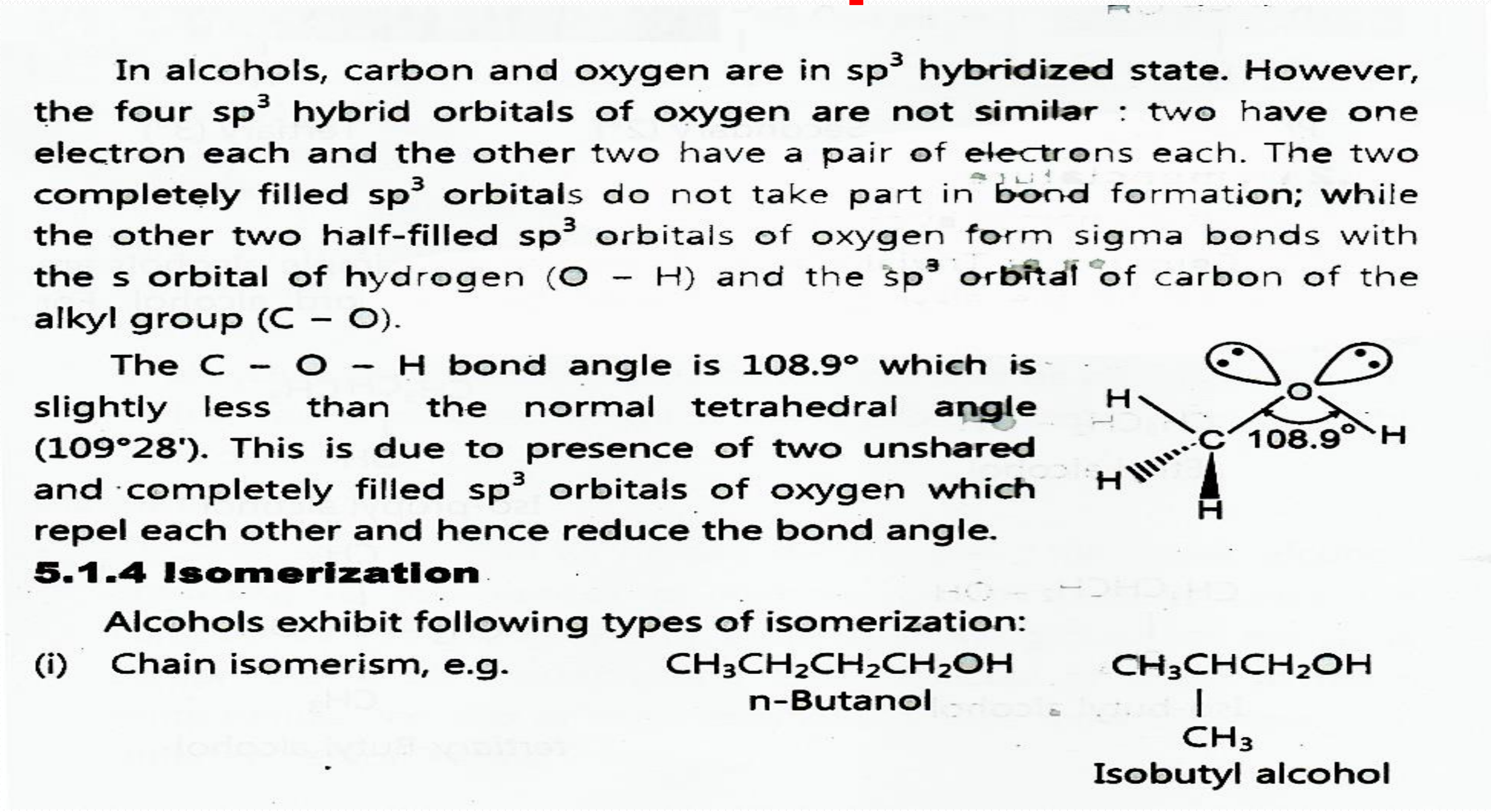
1, 2-Ethanediol



$$\mathrm{CH_3\underset{\underset{CH_3}{|}}{C}HCH_2-OH}$$

2-Methyl-1-propanol

Structure and Shape



In alcohols, carbon and oxygen are in sp^3 hybridized state. However, the four sp^3 hybrid orbitals of oxygen are not similar : two have one electron each and the other two have a pair of electrons each. The two completely filled sp^3 orbitals do not take part in bond formation; while the other two half-filled sp^3 orbitals of oxygen form sigma bonds with the s orbital of hydrogen (O – H) and the sp^3 orbital of carbon of the alkyl group (C – O).

The C – O – H bond angle is 108.9° which is slightly less than the normal tetrahedral angle (109°28'). This is due to presence of two unshared and completely filled sp^3 orbitals of oxygen which repel each other and hence reduce the bond angle.

5.1.4 Isomerization

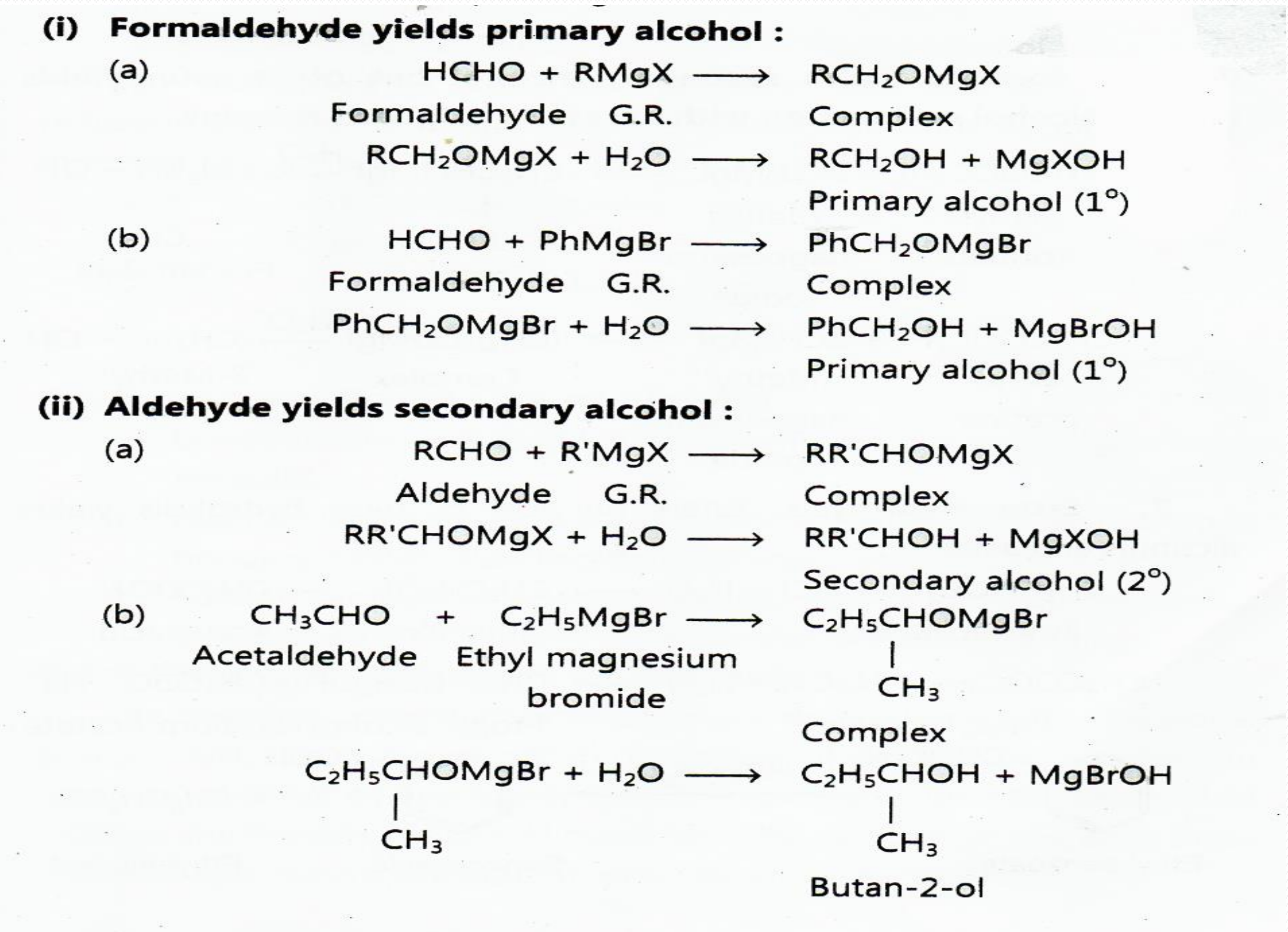
Alcohols exhibit following types of isomerization:

(i) Chain isomerism, e.g. $CH_3CH_2CH_2CH_2OH$ n-Butanol

$$\underset{\displaystyle CH_3}{CH_3\overset{}{C}HCH_2OH}$$

Isobutyl alcohol

Preparation of Alcohol



(i) Formaldehyde yields primary alcohol :

(a)

$$\underset{\text{Formaldehyde}}{HCHO} + \underset{\text{G.R.}}{RMgX} \longrightarrow \underset{\text{Complex}}{RCH_2OMgX}$$

$$RCH_2OMgX + H_2O \longrightarrow \underset{\text{Primary alcohol } (1^\circ)}{RCH_2OH} + MgXOH$$

(b)

$$\underset{\text{Formaldehyde}}{HCHO} + \underset{\text{G.R.}}{PhMgBr} \longrightarrow \underset{\text{Complex}}{PhCH_2OMgBr}$$

$$PhCH_2OMgBr + H_2O \longrightarrow \underset{\text{Primary alcohol } (1^\circ)}{PhCH_2OH} + MgBrOH$$

(ii) Aldehyde yields secondary alcohol :

(a)

$$\underset{\text{Aldehyde}}{RCHO} + \underset{\text{G.R.}}{R'MgX} \longrightarrow \underset{\text{Complex}}{RR'CHOMgX}$$

$$RR'CHOMgX + H_2O \longrightarrow \underset{\text{Secondary alcohol } (2^\circ)}{RR'CHOH} + MgXOH$$

(b)

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + \underset{\text{Ethyl magnesium bromide}}{C_2H_5MgBr} \longrightarrow \underset{\text{Complex}}{C_2H_5\underset{\underset{CH_3}{|}}{C}HOMgBr}$$

$$C_2H_5\underset{\underset{CH_3}{|}}{C}HOMgBr + H_2O \longrightarrow \underset{\text{Butan-2-ol}}{C_2H_5\underset{\underset{CH_3}{|}}{C}HOH} + MgBrOH$$

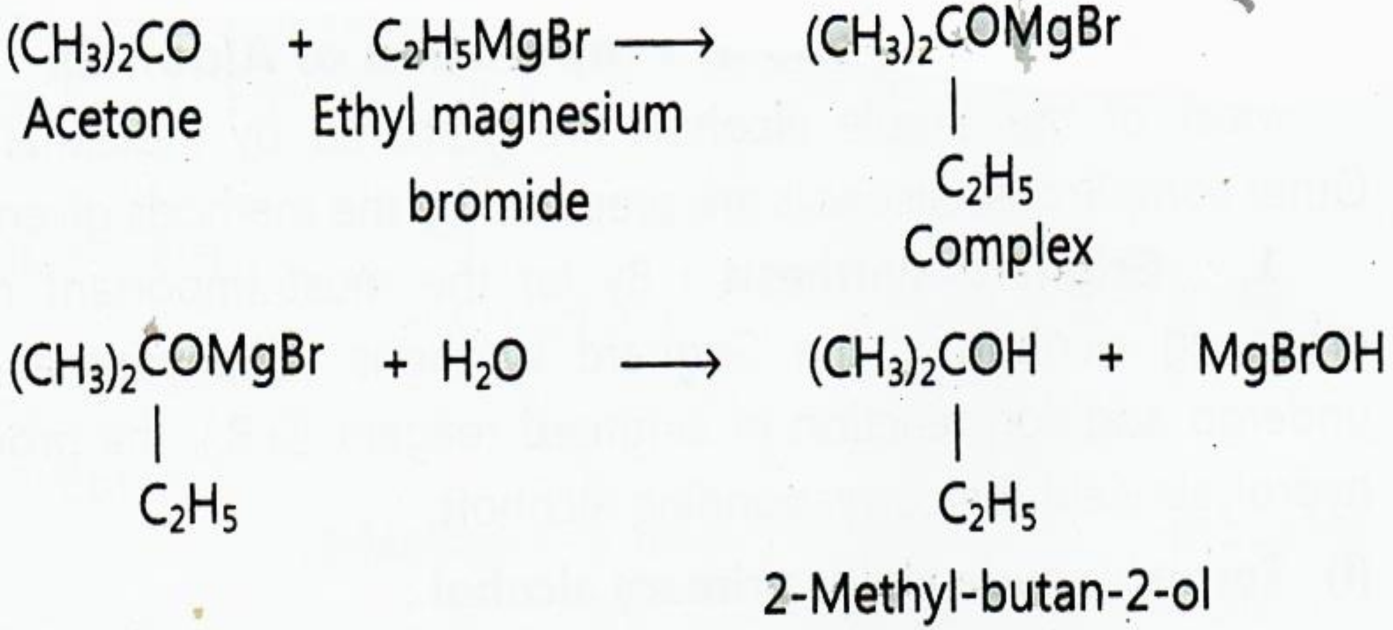
(iii) Ketone yields tertiary alcohol :

(a)

$$\underset{\text{Ketone}}{RR'CO} + \underset{\text{G.R.}}{R''MgX} \longrightarrow \underset{\text{Complex}}{RR'R''COMgX}$$

$$RR'R''COMgX + H_2O \longrightarrow \underset{\text{Tertiary alcohol }(3^\circ)}{RR'R''COH} + MgXOH$$

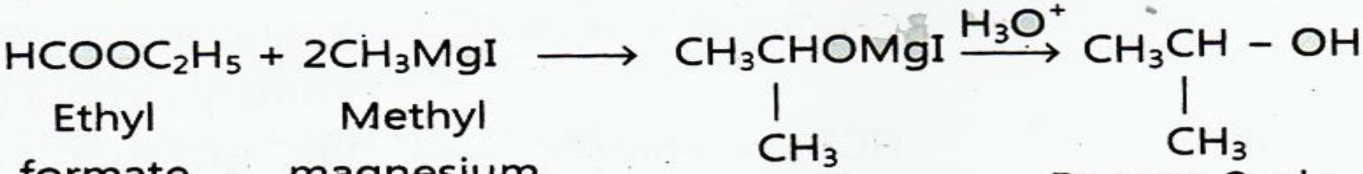
(b)



$$\underset{\text{Acetone}}{(CH_3)_2CO} + \underset{\text{Ethyl magnesium bromide}}{C_2H_5MgBr} \longrightarrow \underset{\text{Complex}}{\underset{C_2H_5}{\overset{|}{(CH_3)_2COMgBr}}}$$

$$\underset{C_2H_5}{\overset{|}{(CH_3)_2COMgBr}} + H_2O \longrightarrow \underset{\text{2-Methyl-butan-2-ol}}{\underset{C_2H_5}{\overset{|}{(CH_3)_2COH}}} + MgBrOH$$

(iv) Ethyl formate yields secondary alcohol but other ester yields tertiary alcohol on reaction with excess of Grignard reagent.



$$HCOOC_2H_5 + 2CH_3MgI \longrightarrow \underset{\underset{CH_3}{|}}{CH_3CHOMgI} \xrightarrow{H_3O^+} \underset{\underset{CH_3}{|}}{CH_3CH} - OH$$

Ethyl formate | Methyl magnesium iodide | Complex | Propan-2-ol

$$CH_3COOC_2H_5 + 2CH_3MgI \longrightarrow (CH_3)_3COMgI \xrightarrow{H_3O^+} (CH_3)_3C - OH$$

Ethyl acetate | Methyl magnesium iodide | Complex | 2-Methyl-propan-2-ol

2. Ester Hydrolysis: Esters on acid or base hydrolysis yields alcohols and acids

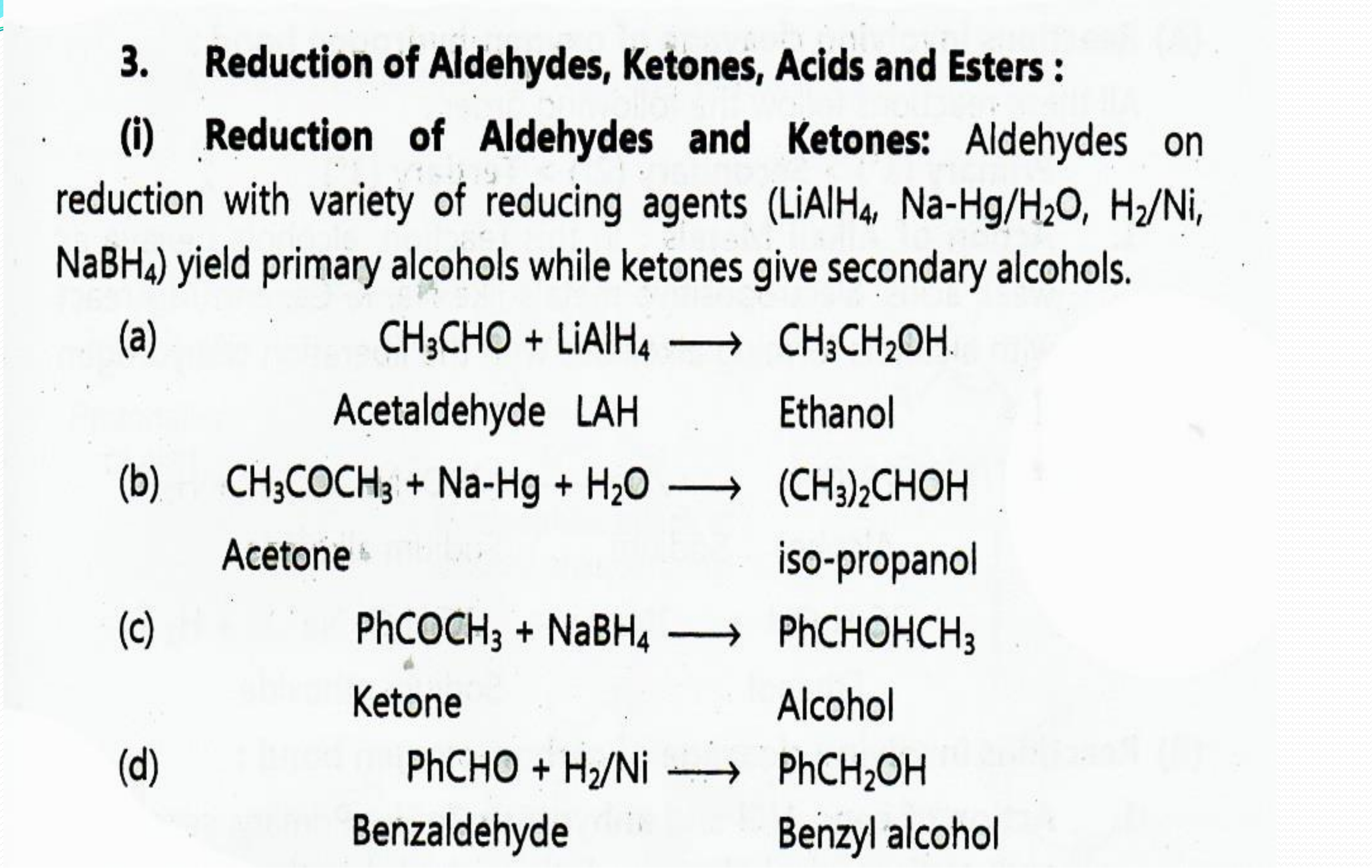
$$CH_3COOC_2H_5 + HCl + H_2O \longrightarrow CH_3CH_2OH + CH_3COOH$$

Ethyl acetate | Ethyl alcohol | Acetic acid

$$CH_3COOC_3H_7 + NaOH + H_2O \longrightarrow CH_3CH_2CH_2OH + CH_3COO^- Na^+$$

Propyl acetate | Propyl alcohol | Sodium Acetate

Ethyl benzoate | Benzoic acid | Ethyl alcohol



3. Reduction of Aldehydes, Ketones, Acids and Esters :

(i) Reduction of Aldehydes and Ketones: Aldehydes on reduction with variety of reducing agents ($LiAlH_4$, $Na\text{-}Hg/H_2O$, H_2/Ni, $NaBH_4$) yield primary alcohols while ketones give secondary alcohols.

(a) $CH_3CHO + LiAlH_4 \longrightarrow CH_3CH_2OH$

Acetaldehyde LAH Ethanol

(b) $CH_3COCH_3 + Na\text{-}Hg + H_2O \longrightarrow (CH_3)_2CHOH$

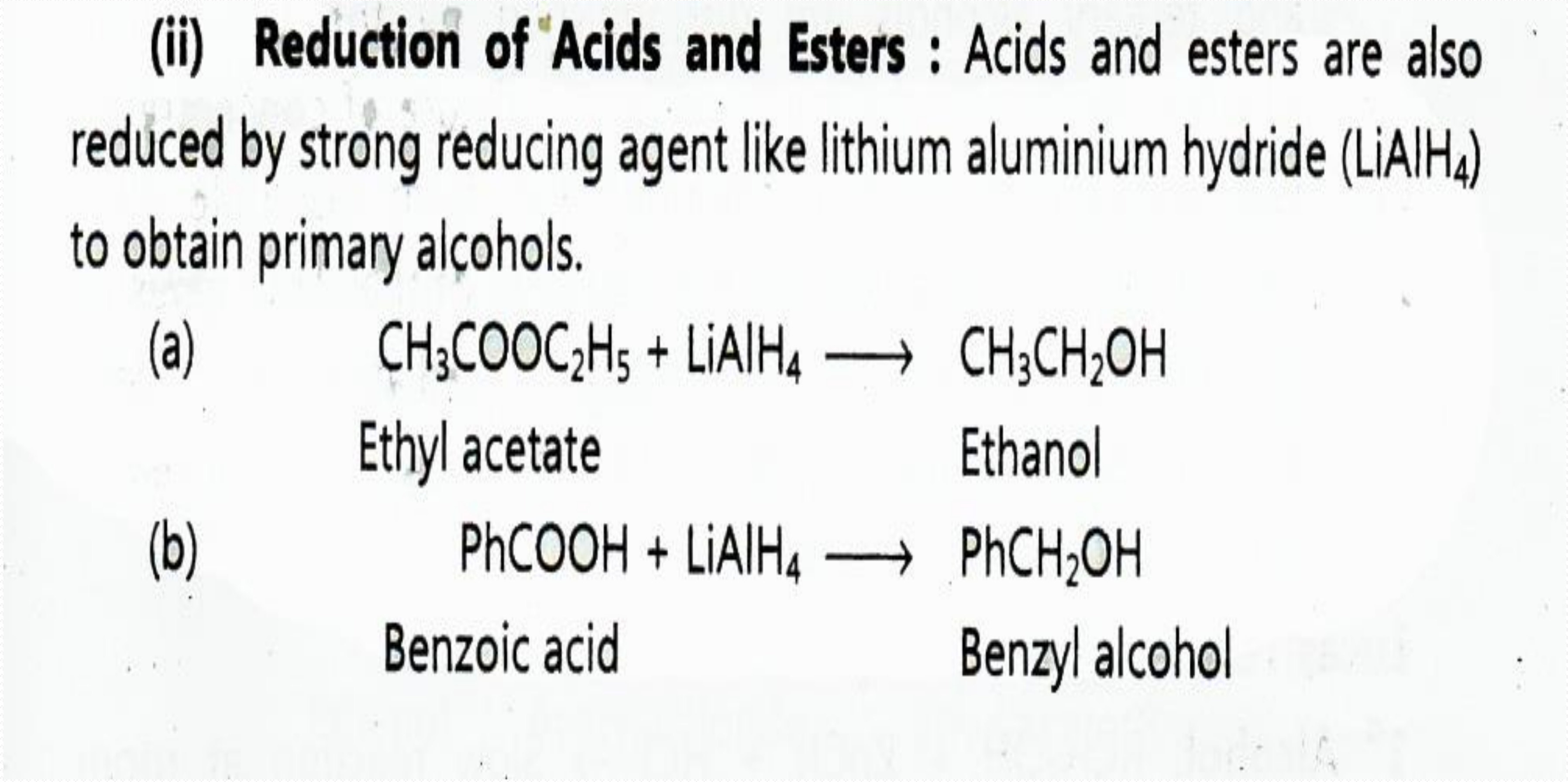
Acetone iso-propanol

(c) $PhCOCH_3 + NaBH_4 \longrightarrow PhCHOHCH_3$

Ketone Alcohol

(d) $PhCHO + H_2/Ni \longrightarrow PhCH_2OH$

Benzaldehyde Benzyl alcohol



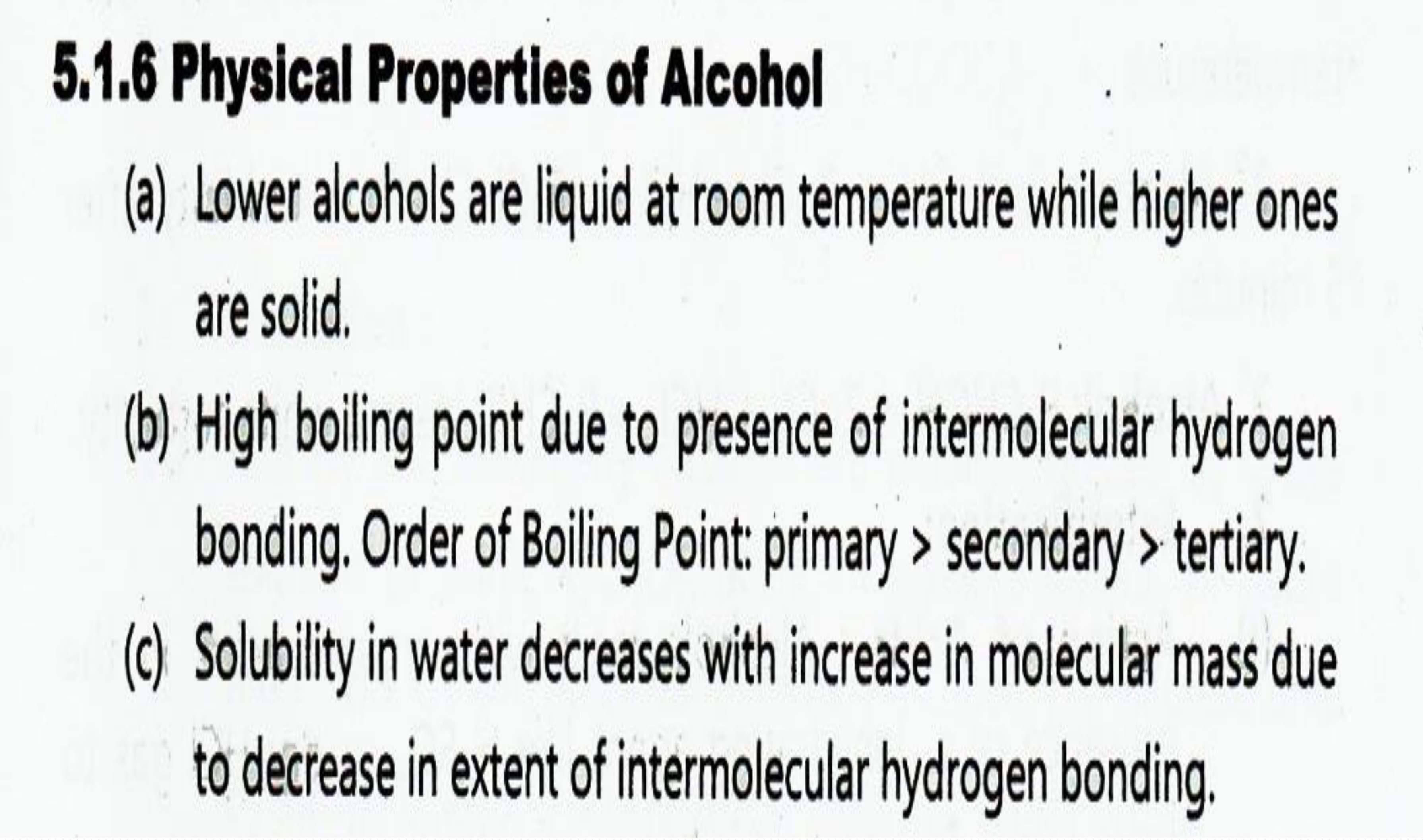
(ii) Reduction of Acids and Esters : Acids and esters are also reduced by strong reducing agent like lithium aluminium hydride ($LiAlH_4$) to obtain primary alcohols.

(a) $CH_3COOC_2H_5 + LiAlH_4 \longrightarrow CH_3CH_2OH$

Ethyl acetate — Ethanol

(b) $PhCOOH + LiAlH_4 \longrightarrow PhCH_2OH$

Benzoic acid — Benzyl alcohol

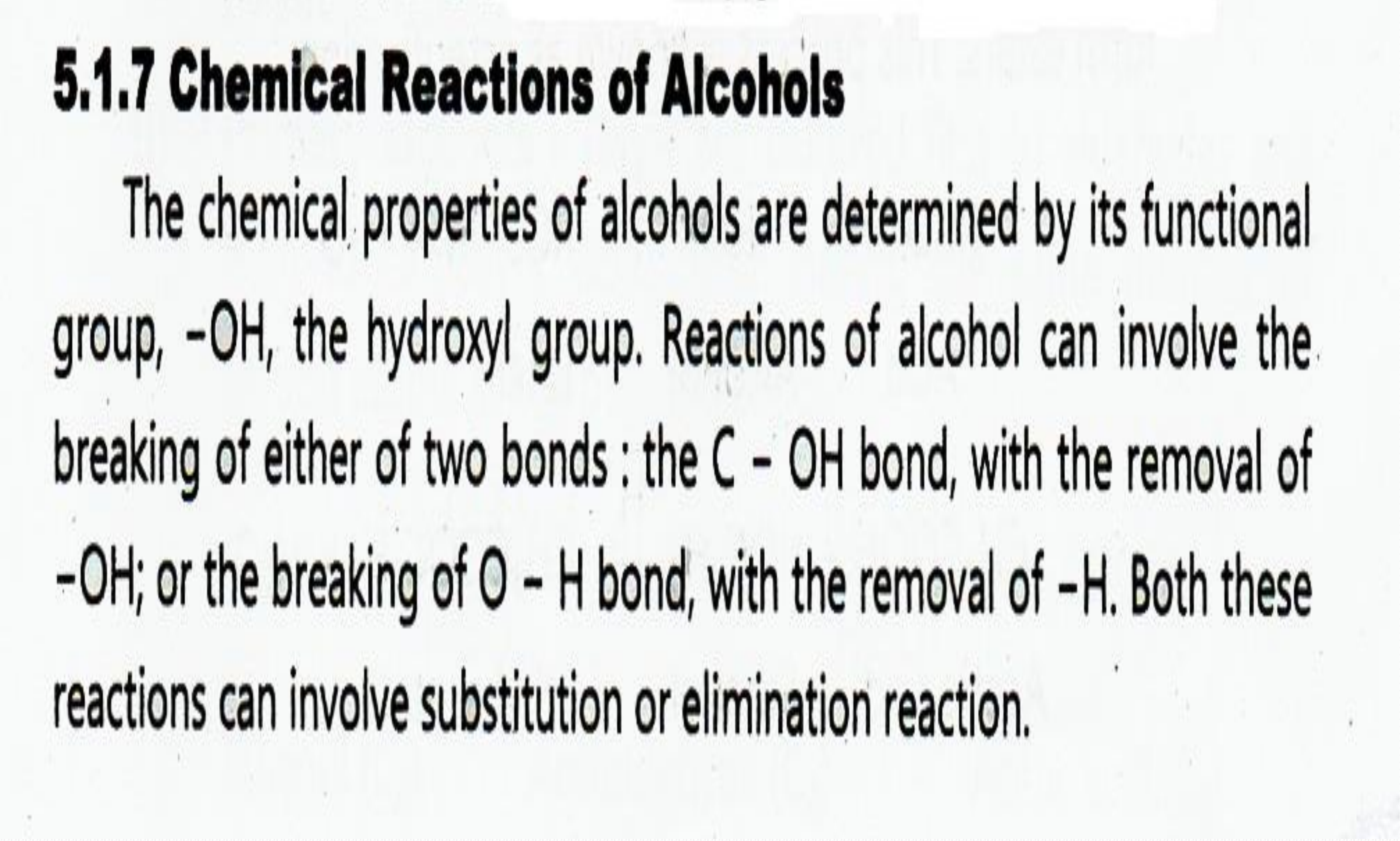


5.1.6 Physical Properties of Alcohol

(a) Lower alcohols are liquid at room temperature while higher ones are solid.

(b) High boiling point due to presence of intermolecular hydrogen bonding. Order of Boiling Point: primary > secondary > tertiary.

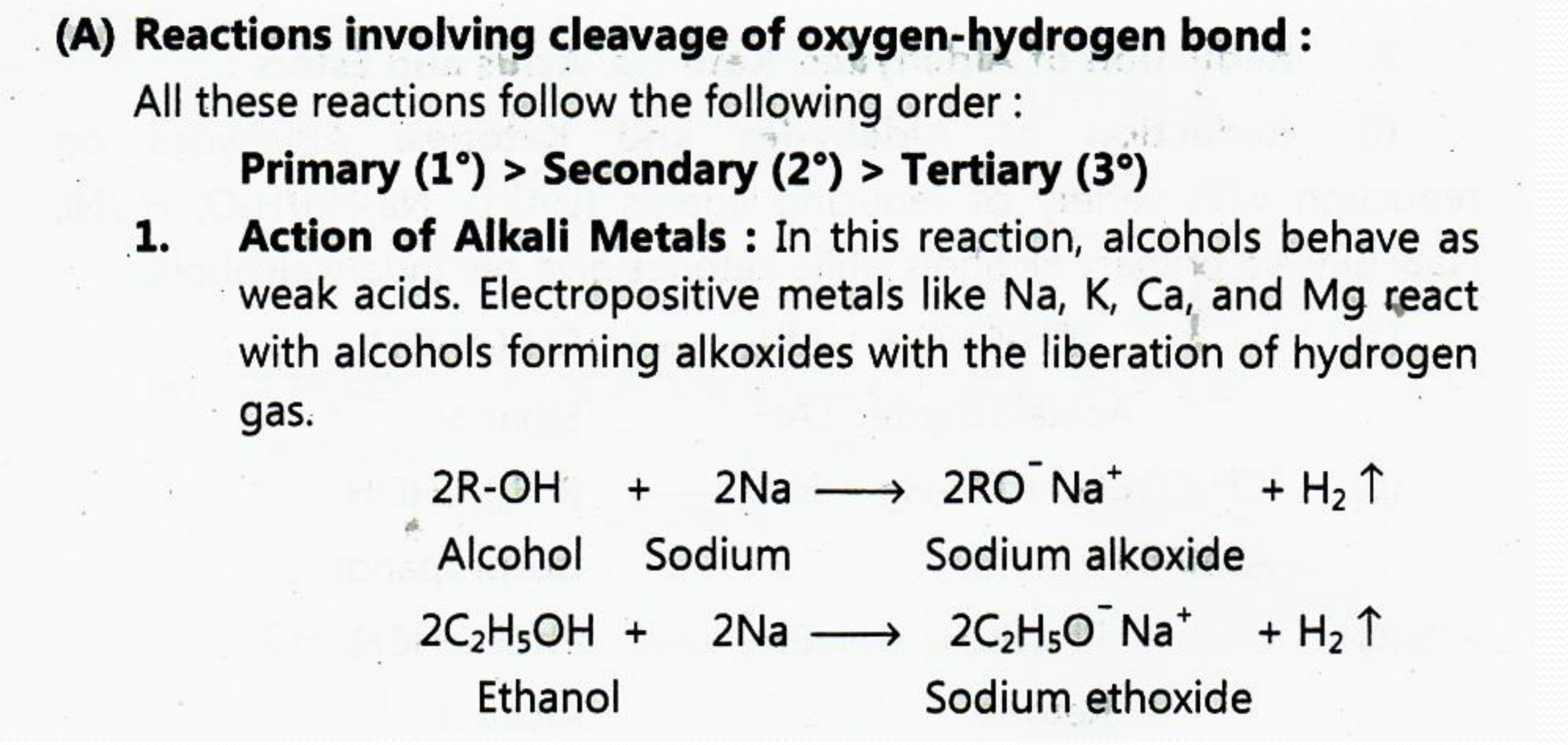
(c) Solubility in water decreases with increase in molecular mass due to decrease in extent of intermolecular hydrogen bonding.



5.1.7 Chemical Reactions of Alcohols

The chemical properties of alcohols are determined by its functional group, –OH, the hydroxyl group. Reactions of alcohol can involve the breaking of either of two bonds : the C – OH bond, with the removal of –OH; or the breaking of O – H bond, with the removal of –H. Both these reactions can involve substitution or elimination reaction.

Cleavage of O and H



(A) Reactions involving cleavage of oxygen-hydrogen bond :

All these reactions follow the following order :

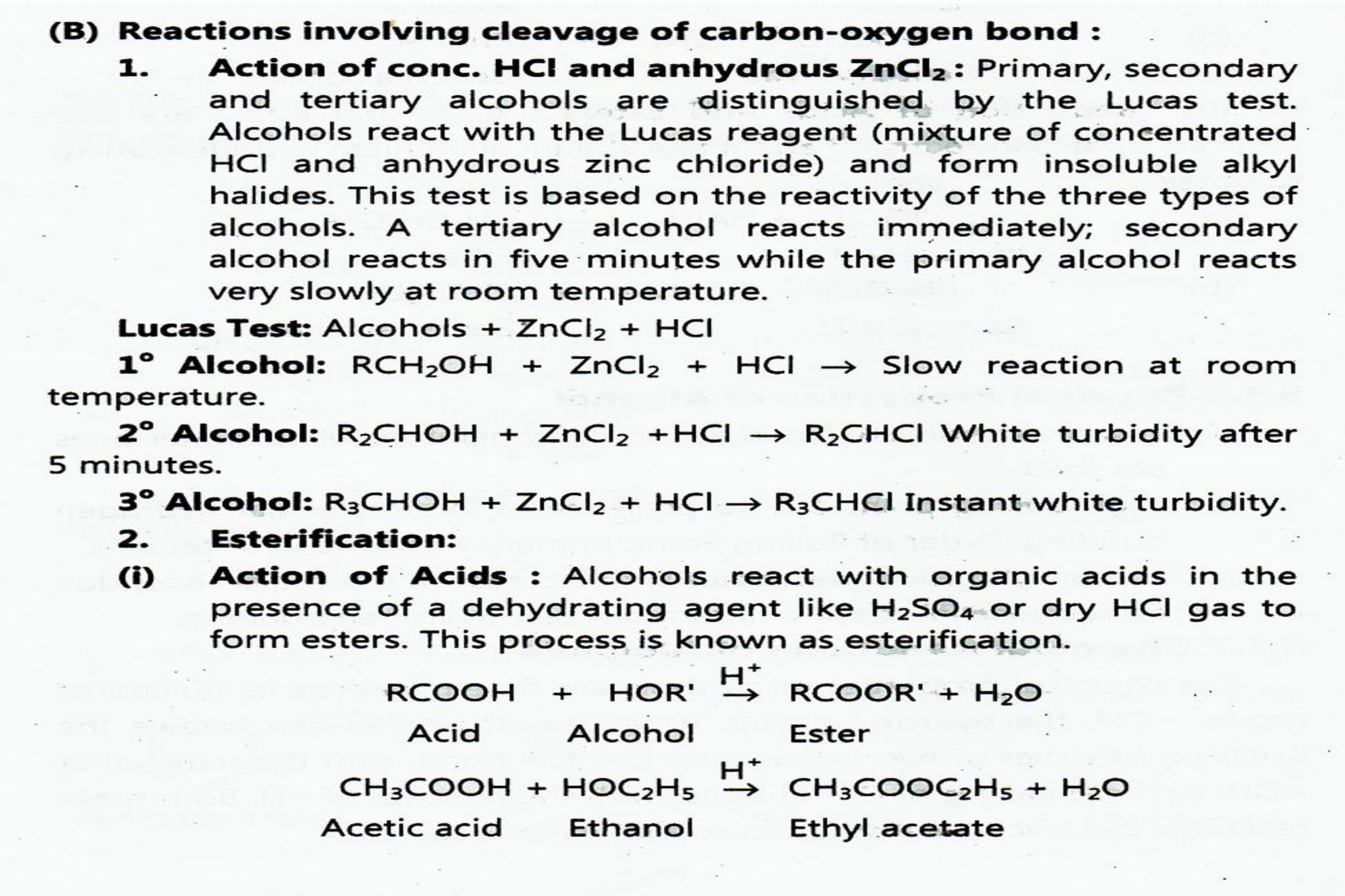
Primary (1°) > Secondary (2°) > Tertiary (3°)

1. **Action of Alkali Metals :** In this reaction, alcohols behave as weak acids. Electropositive metals like Na, K, Ca, and Mg react with alcohols forming alkoxides with the liberation of hydrogen gas.

$$\underset{\text{Alcohol}}{2R\text{-}OH} + \underset{\text{Sodium}}{2Na} \longrightarrow \underset{\text{Sodium alkoxide}}{2RO^{-}Na^{+}} + H_2\uparrow$$

$$\underset{\text{Ethanol}}{2C_2H_5OH} + 2Na \longrightarrow \underset{\text{Sodium ethoxide}}{2C_2H_5O^{-}Na^{+}} + H_2\uparrow$$

Cleavage of O and H



(B) Reactions involving cleavage of carbon-oxygen bond :

1. **Action of conc. HCl and anhydrous $ZnCl_2$:** Primary, secondary and tertiary alcohols are distinguished by the Lucas test. Alcohols react with the Lucas reagent (mixture of concentrated HCl and anhydrous zinc chloride) and form insoluble alkyl halides. This test is based on the reactivity of the three types of alcohols. A tertiary alcohol reacts immediately; secondary alcohol reacts in five minutes while the primary alcohol reacts very slowly at room temperature.

Lucas Test: Alcohols + $ZnCl_2$ + HCl

1° Alcohol: $RCH_2OH + ZnCl_2 + HCl \rightarrow$ Slow reaction at room temperature.

2° Alcohol: $R_2CHOH + ZnCl_2 + HCl \rightarrow R_2CHCl$ White turbidity after 5 minutes.

3° Alcohol: $R_3CHOH + ZnCl_2 + HCl \rightarrow R_3CHCl$ Instant white turbidity.

2. **Esterification:**

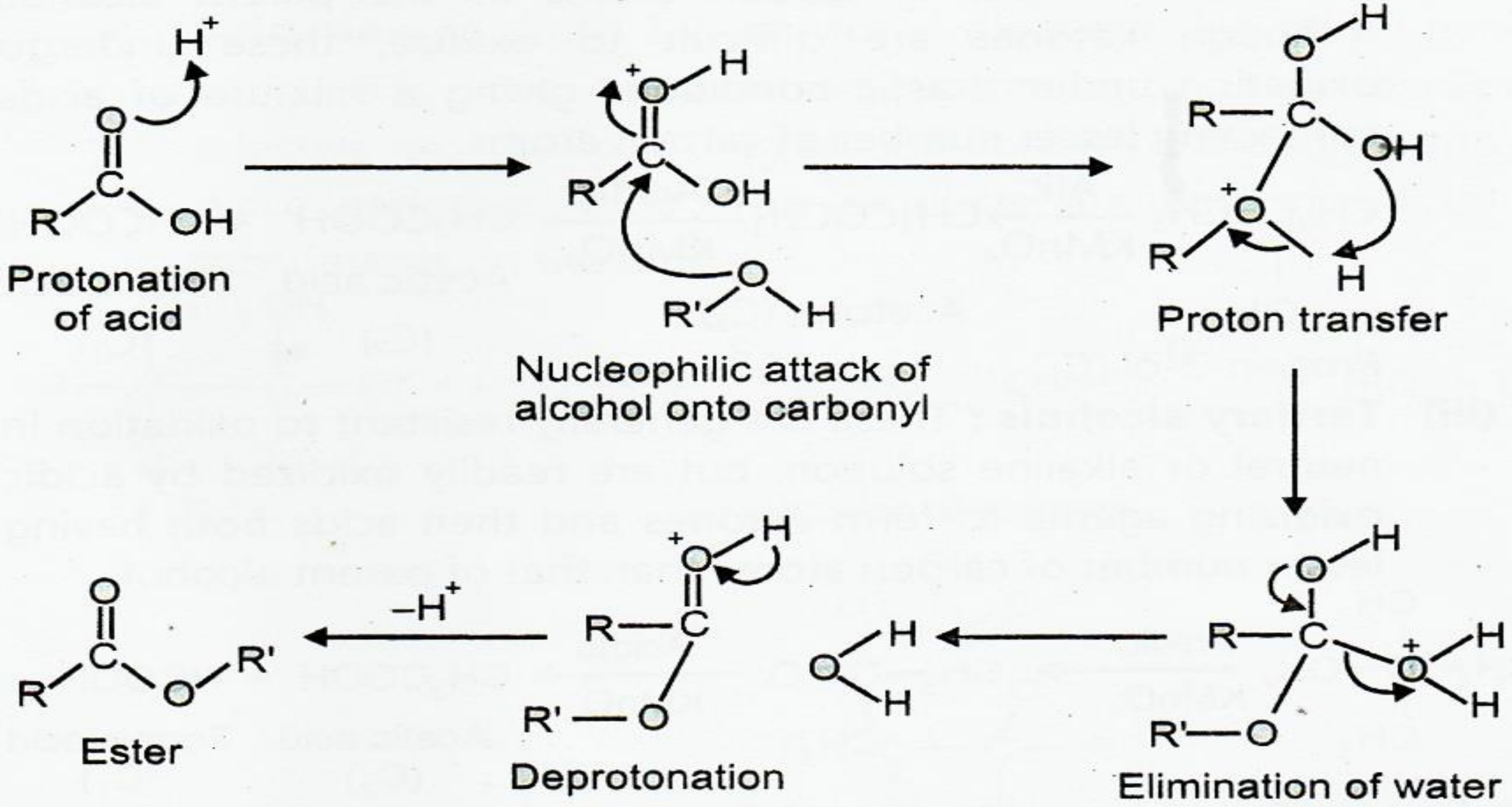
(i) **Action of Acids :** Alcohols react with organic acids in the presence of a dehydrating agent like H_2SO_4 or dry HCl gas to form esters. This process is known as esterification.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Alcohol}}{HOR'} \xrightarrow{H^+} \underset{\text{Ester}}{RCOOR'} + H_2O$$

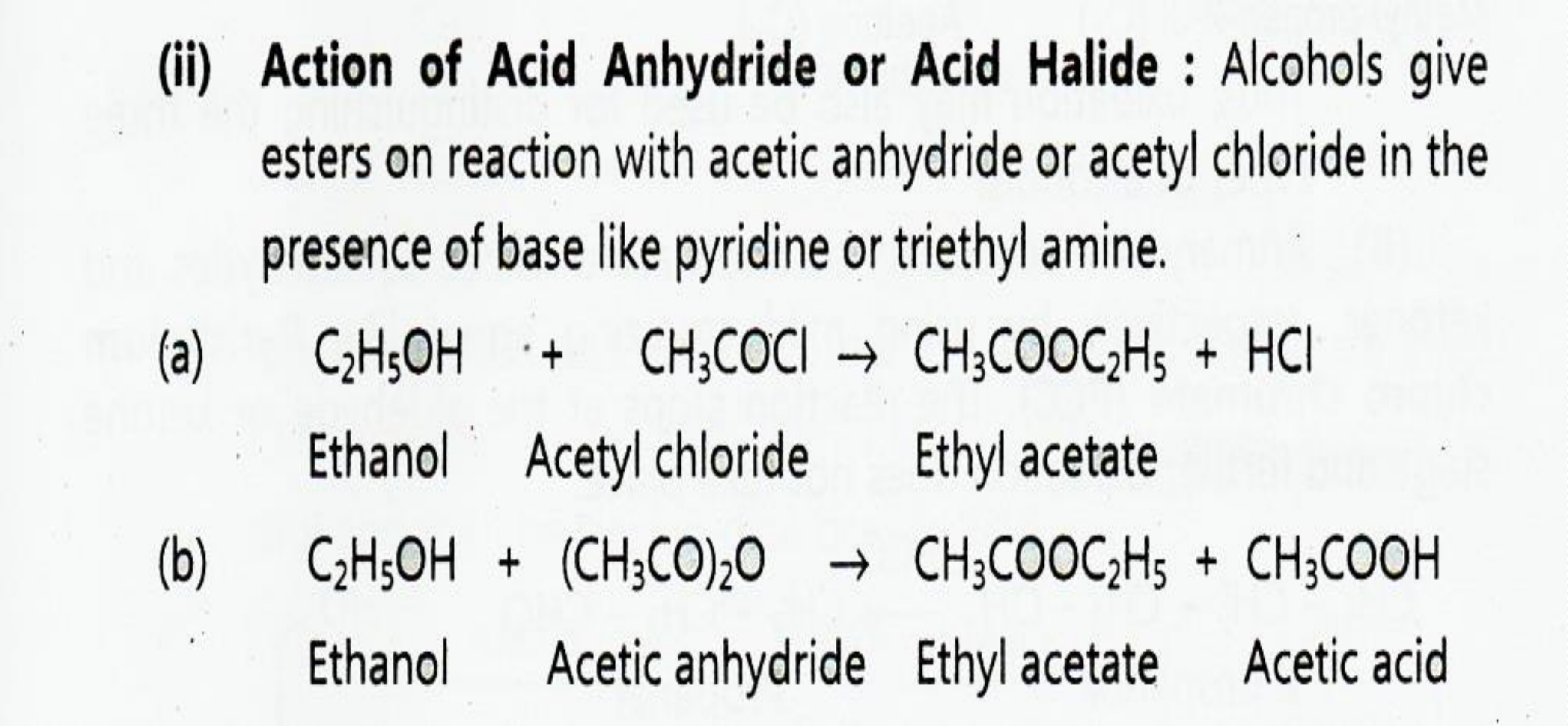
$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{HOC_2H_5} \xrightarrow{H^+} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Mechanism

Mechanism : The reaction follows the following path :



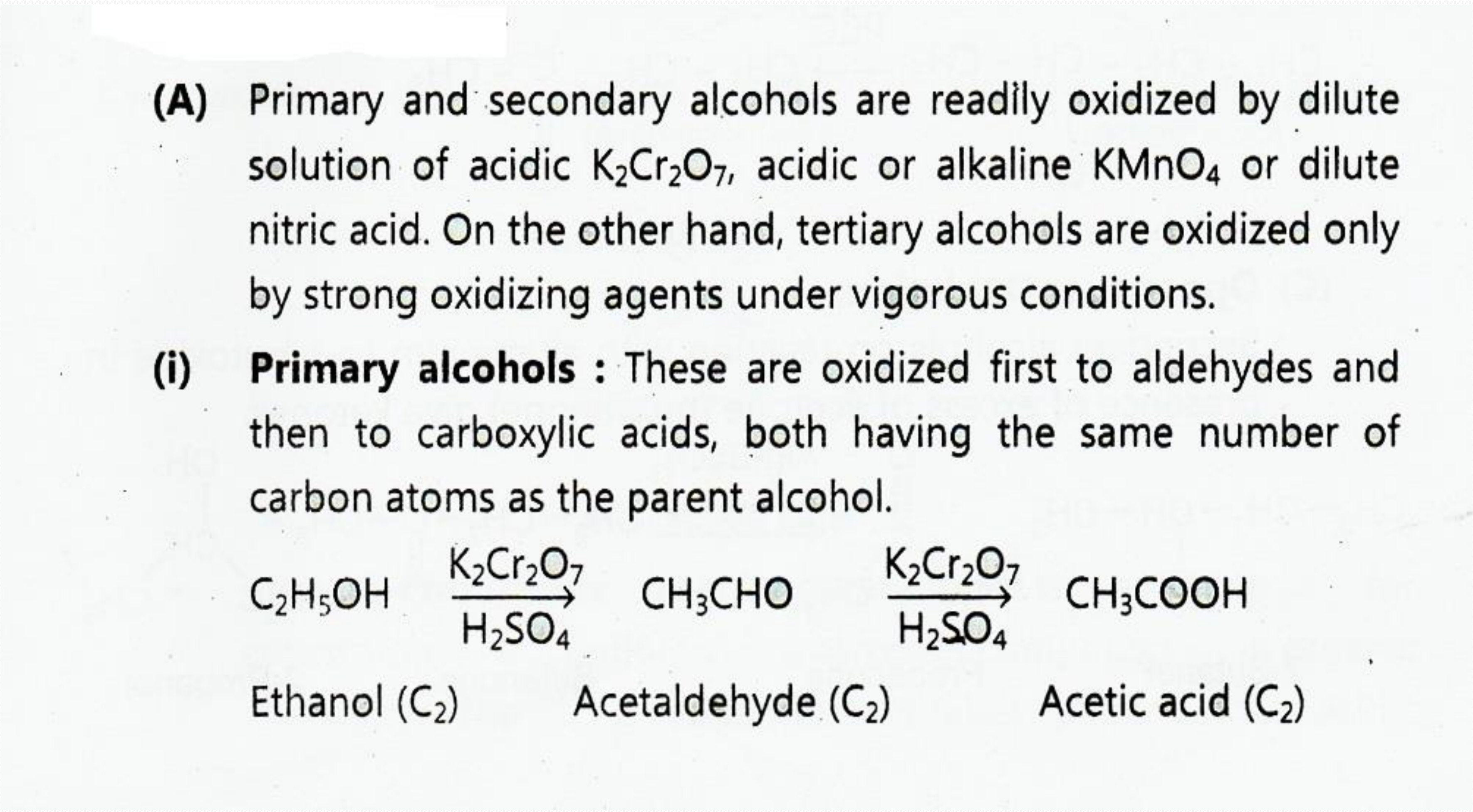
Action of Acid Halide or Acid Anhydride



(ii) **Action of Acid Anhydride or Acid Halide :** Alcohols give esters on reaction with acetic anhydride or acetyl chloride in the presence of base like pyridine or triethyl amine.

(a)	C_2H_5OH	+	CH_3COCl	$\rightarrow$	$CH_3COOC_2H_5$	+	HCl	
	Ethanol		Acetyl chloride		Ethyl acetate			
(b)	C_2H_5OH	+	$(CH_3CO)_2O$	$\rightarrow$	$CH_3COOC_2H_5$	+	CH_3COOH	
	Ethanol		Acetic anhydride		Ethyl acetate		Acetic acid	

Oxidation

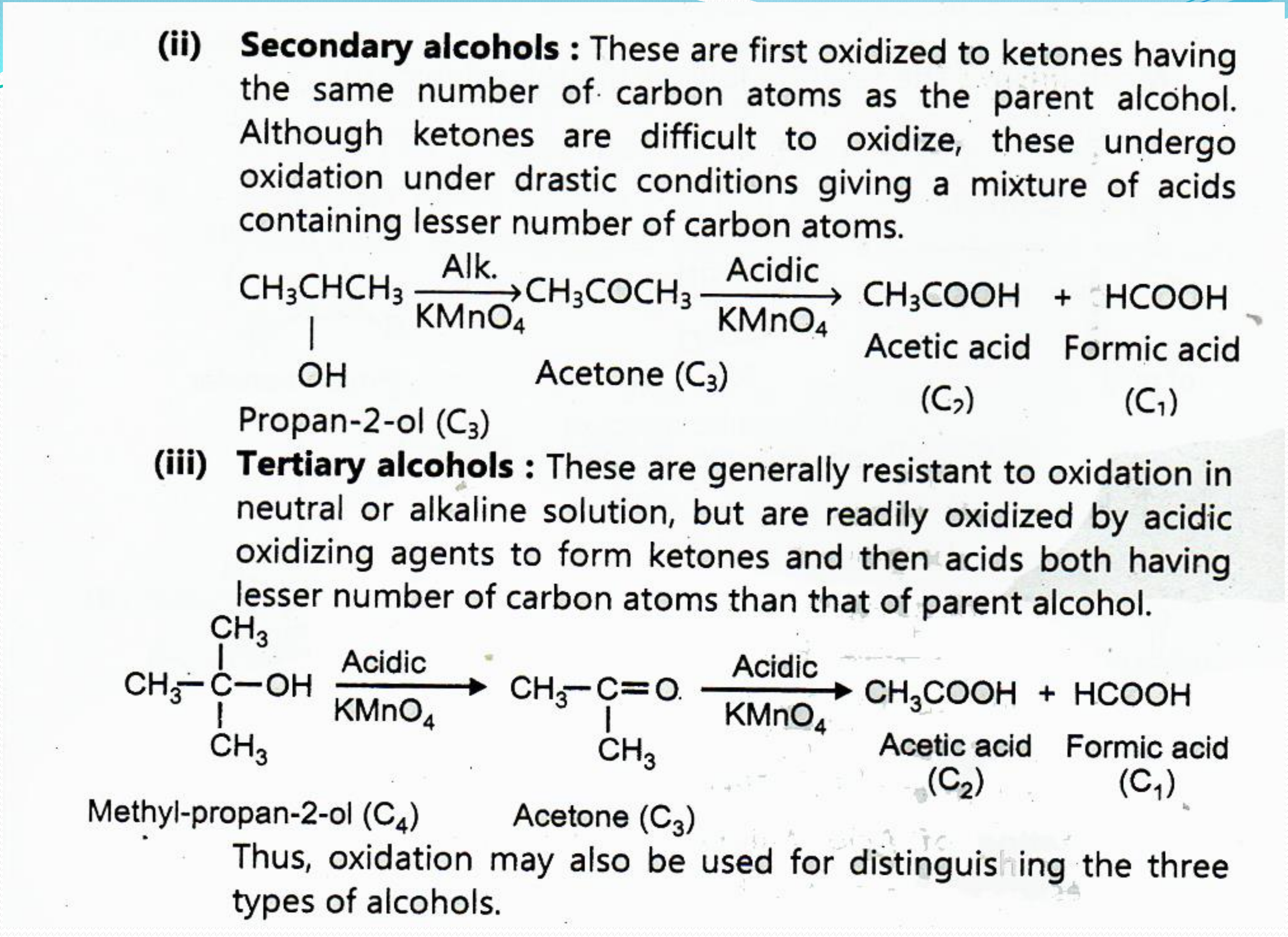


(A) Primary and secondary alcohols are readily oxidized by dilute solution of acidic $K_2Cr_2O_7$, acidic or alkaline $KMnO_4$ or dilute nitric acid. On the other hand, tertiary alcohols are oxidized only by strong oxidizing agents under vigorous conditions.

(i) **Primary alcohols :** These are oxidized first to aldehydes and then to carboxylic acids, both having the same number of carbon atoms as the parent alcohol.

$$C_2H_5OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3CHO \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3COOH$$

Ethanol (C_2) Acetaldehyde (C_2) Acetic acid (C_2)



(ii) **Secondary alcohols :** These are first oxidized to ketones having the same number of carbon atoms as the parent alcohol. Although ketones are difficult to oxidize, these undergo oxidation under drastic conditions giving a mixture of acids containing lesser number of carbon atoms.

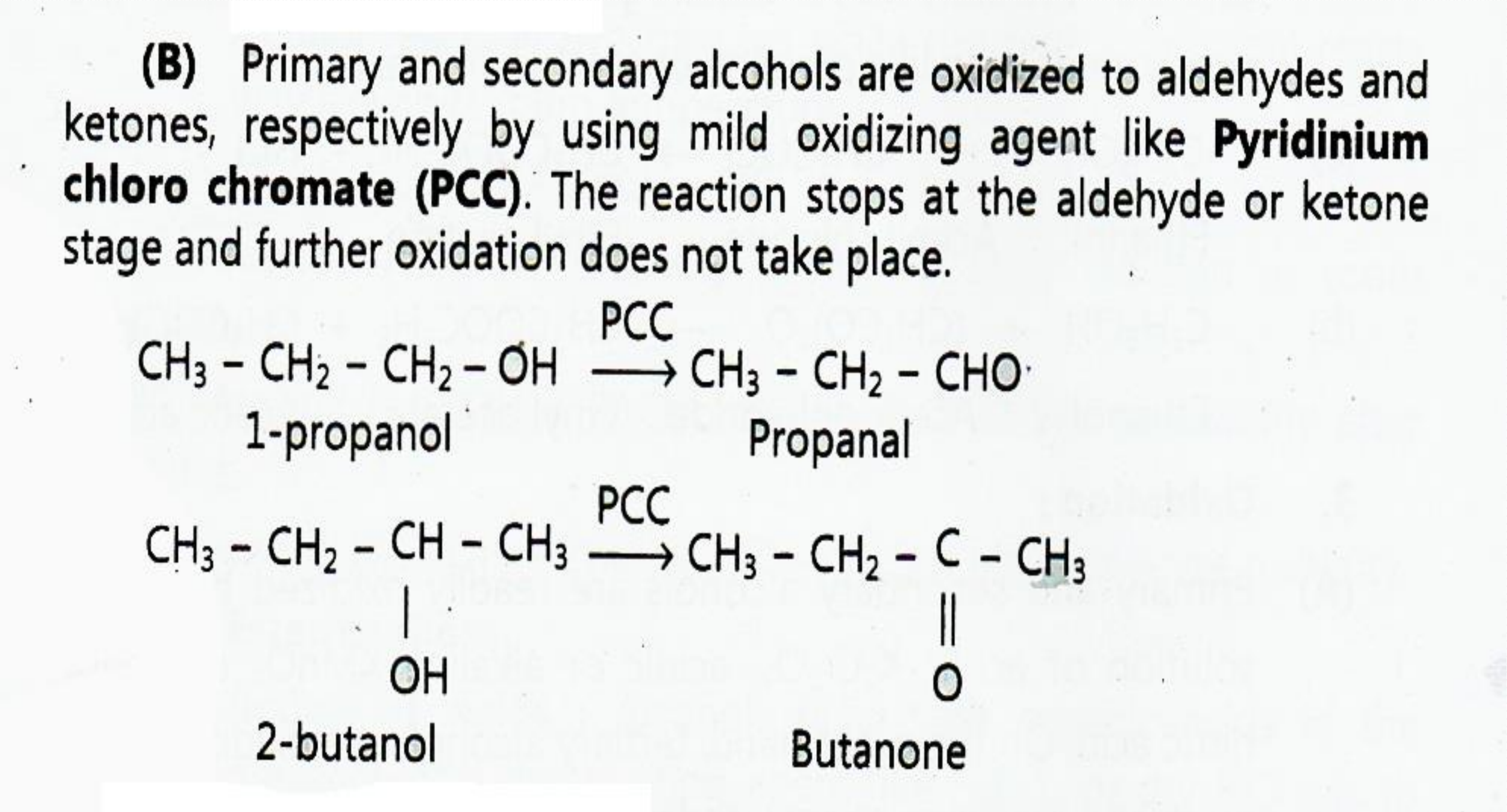
$$\underset{\text{Propan-2-ol }(C_3)}{\mathrm{CH_3\underset{\underset{OH}{|}}{C}HCH_3}} \xrightarrow[\mathrm{KMnO_4}]{\text{Alk.}} \underset{\text{Acetone }(C_3)}{\mathrm{CH_3COCH_3}} \xrightarrow[\mathrm{KMnO_4}]{\text{Acidic}} \underset{\substack{\text{Acetic acid}\\(C_2)}}{\mathrm{CH_3COOH}} + \underset{\substack{\text{Formic acid}\\(C_1)}}{\mathrm{HCOOH}}$$

(iii) **Tertiary alcohols :** These are generally resistant to oxidation in neutral or alkaline solution, but are readily oxidized by acidic oxidizing agents to form ketones and then acids both having lesser number of carbon atoms than that of parent alcohol.

$$\underset{\text{Methyl-propan-2-ol }(C_4)}{\mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{-}OH}} \xrightarrow[\mathrm{KMnO_4}]{\text{Acidic}} \underset{\text{Acetone }(C_3)}{\mathrm{CH_3{-}\underset{\underset{CH_3}{|}}{C}{=}O}} \xrightarrow[\mathrm{KMnO_4}]{\text{Acidic}} \underset{\substack{\text{Acetic acid}\\(C_2)}}{\mathrm{CH_3COOH}} + \underset{\substack{\text{Formic acid}\\(C_1)}}{\mathrm{HCOOH}}$$

Thus, oxidation may also be used for distinguishing the three types of alcohols.

PCC

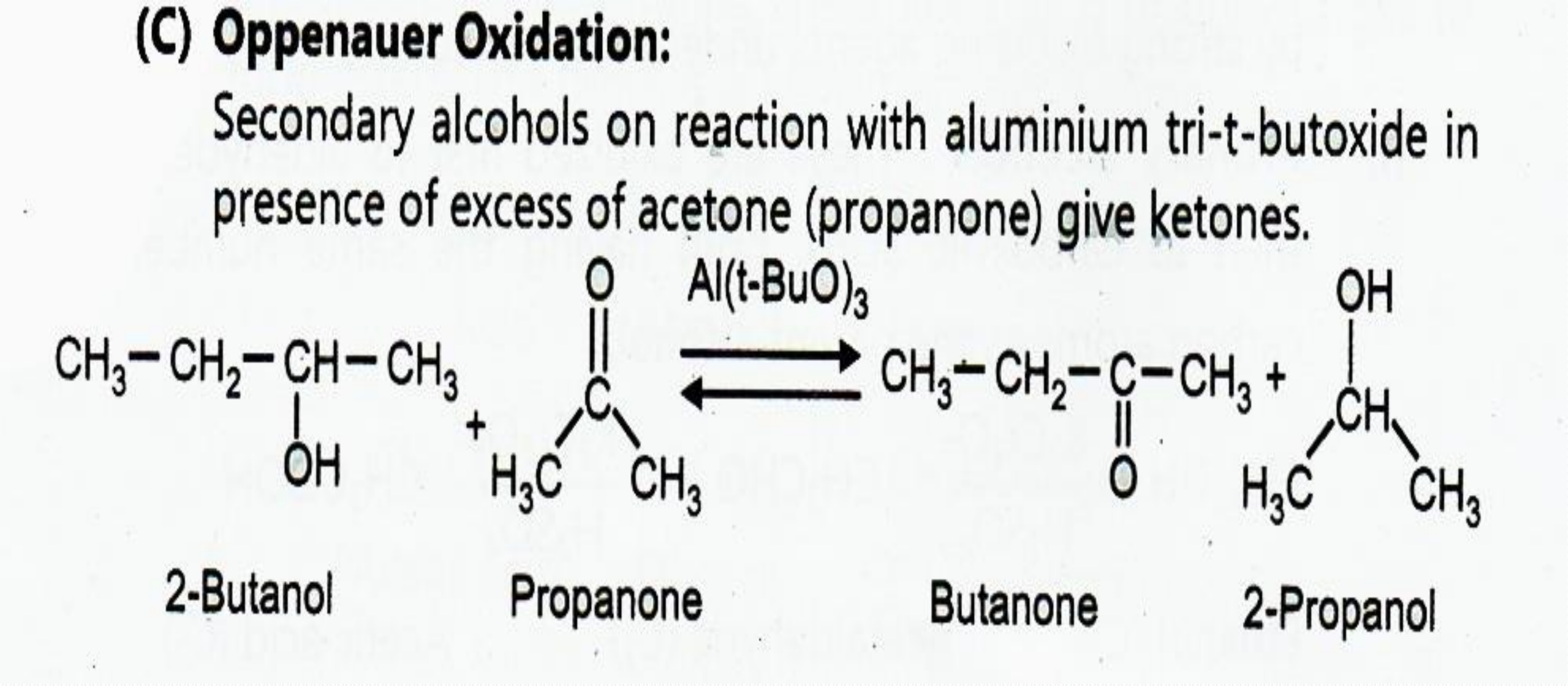


(B) Primary and secondary alcohols are oxidized to aldehydes and ketones, respectively by using mild oxidizing agent like **Pyridinium chloro chromate (PCC)**. The reaction stops at the aldehyde or ketone stage and further oxidation does not take place.

$$\underset{\text{1-propanol}}{CH_3-CH_2-CH_2-OH} \xrightarrow{PCC} \underset{\text{Propanal}}{CH_3-CH_2-CHO}$$

$$\underset{\text{2-butanol}}{CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3} \xrightarrow{PCC} \underset{\text{Butanone}}{CH_3-CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3}$$

Oppenauer Oxidation



(C) Oppenauer Oxidation:

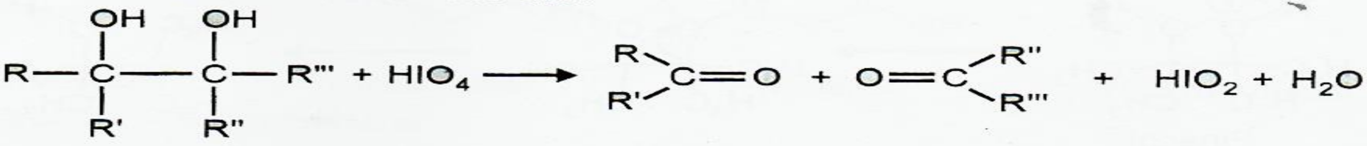
Secondary alcohols on reaction with aluminium tri-t-butoxide in presence of excess of acetone (propanone) give ketones.

$Al(t\text{-}BuO)_3$

2-Butanol + Propanone ⇌ Butanone + 2-Propanol

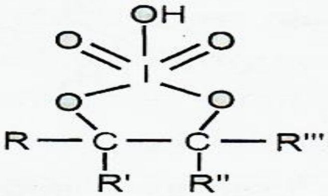
Diols

- **Oxidation of diols:** 1,2- or vicinal diols are cleaved by periodic acid, HIO_4, into two carbonyl compounds. The reaction is selective for 1,2-diols. The reaction occurs via the formation of a cyclic periodate ester. The products are determined by the substituents on the diol.



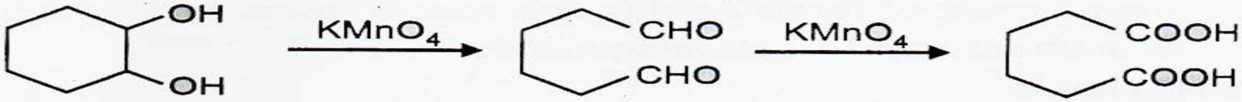
1, 2-diol

2 Molecules of ketones



Periodate ester

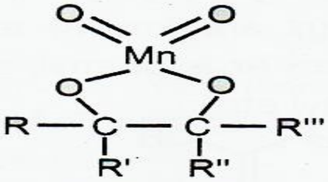
- 1,2- or vicinal diols are also cleaved by $KMnO_4$, initially into two carbonyl compounds. The reaction is also selective for 1,2-diols. The reaction occurs via the formation of a cyclic mangnate ester. Cyclohexane on reaction with $KMnO_4$ initially gives hexan-1,6-diol and then hexan-1,6-dicarboxylic acid.



Cyclohexane-1, 2-diol

Hexan-1, 6-diol
(Adipaldehyde)

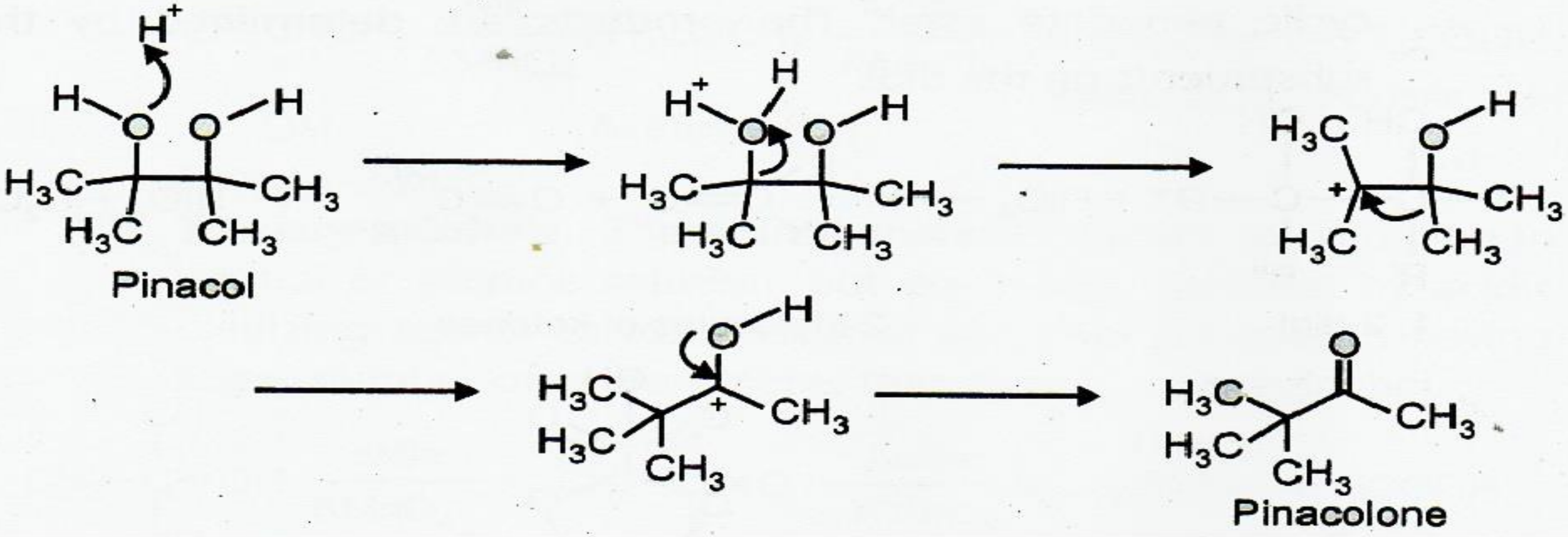
Hexan-1, 6-dicarboxylic acid
(Adipic acid)



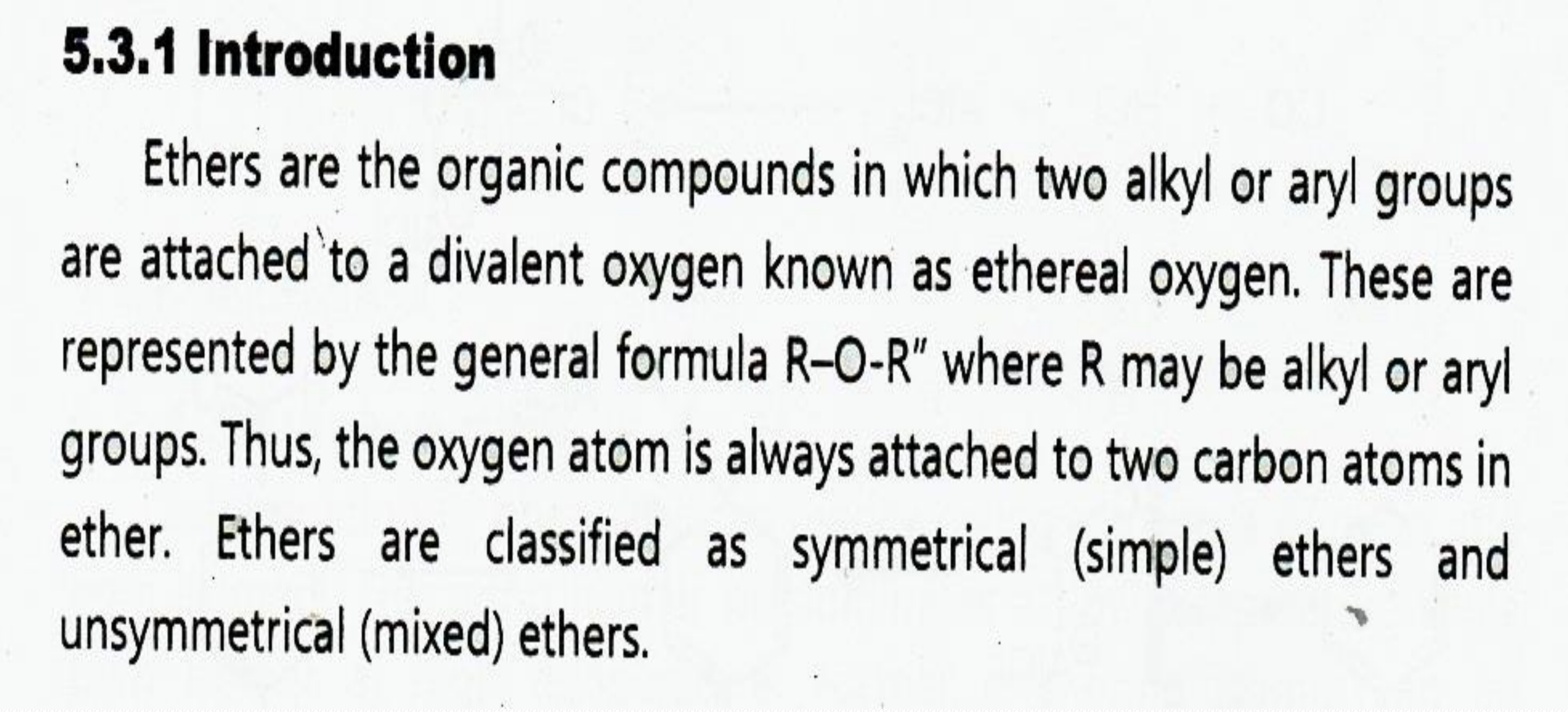
Manganate ester

Pinacol-Pinacolone Rearrangement

- **Pinacol-Pinacolone rearrangement:** It is a method for converting a 1,2-diol to a carbonyl compound in organic chemistry. The 1, 2-rearrangement takes place under acidic conditions. The name of the rearrangement reaction comes from the rearrangement of pinacol to pinacolone. It is important to note that this rearrangement is regioselective in nature. The rearrangement of the more stable carbocation yields the major product.



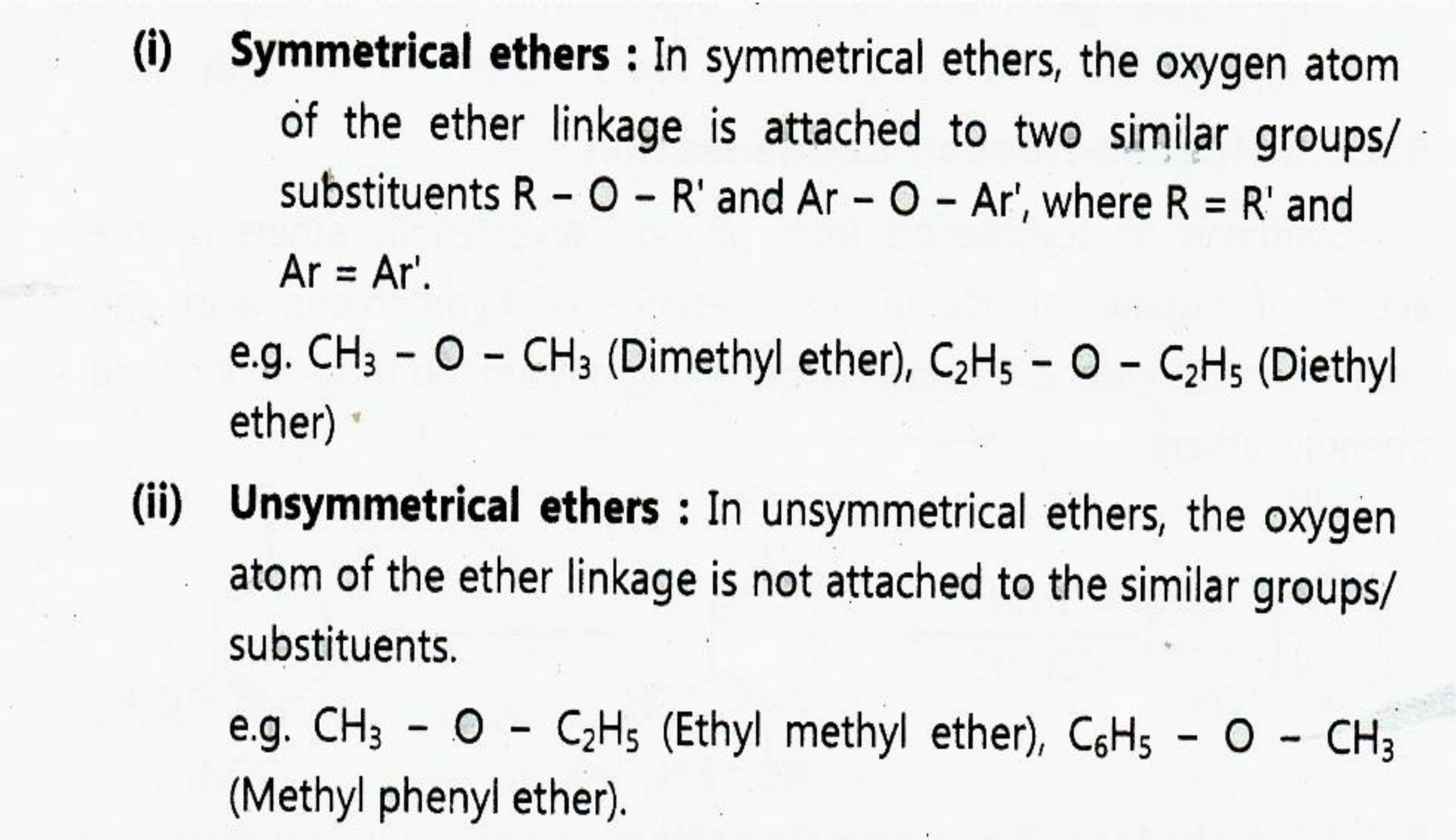
ETHERS



5.3.1 Introduction

Ethers are the organic compounds in which two alkyl or aryl groups are attached to a divalent oxygen known as ethereal oxygen. These are represented by the general formula R–O-R″ where R may be alkyl or aryl groups. Thus, the oxygen atom is always attached to two carbon atoms in ether. Ethers are classified as symmetrical (simple) ethers and unsymmetrical (mixed) ethers.

Classification of Ether



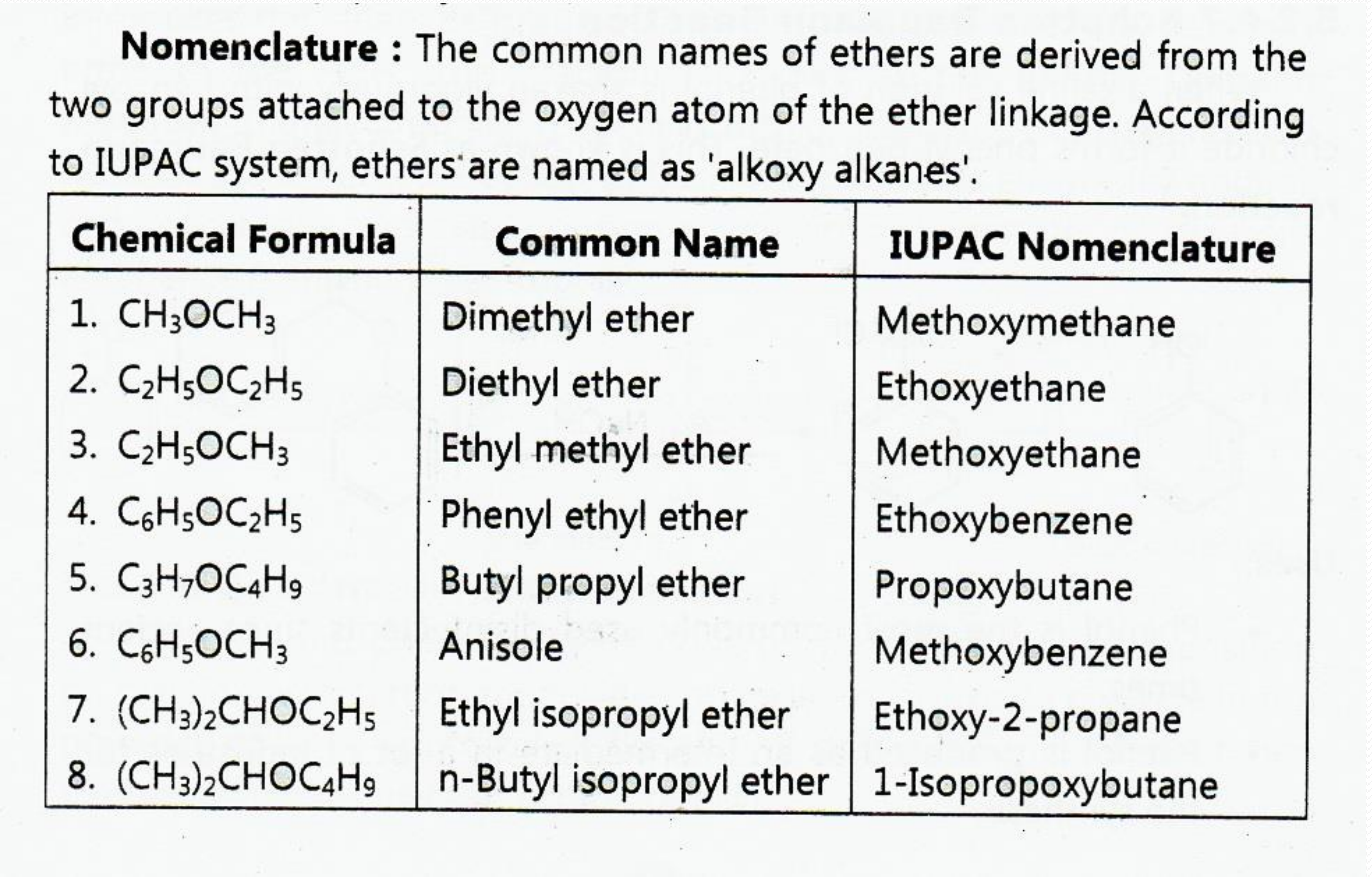
(i) **Symmetrical ethers :** In symmetrical ethers, the oxygen atom of the ether linkage is attached to two similar groups/ substituents R – O – R' and Ar – O – Ar', where R = R' and Ar = Ar'.

e.g. $CH_3 - O - CH_3$ (Dimethyl ether), $C_2H_5 - O - C_2H_5$ (Diethyl ether)

(ii) **Unsymmetrical ethers :** In unsymmetrical ethers, the oxygen atom of the ether linkage is not attached to the similar groups/ substituents.

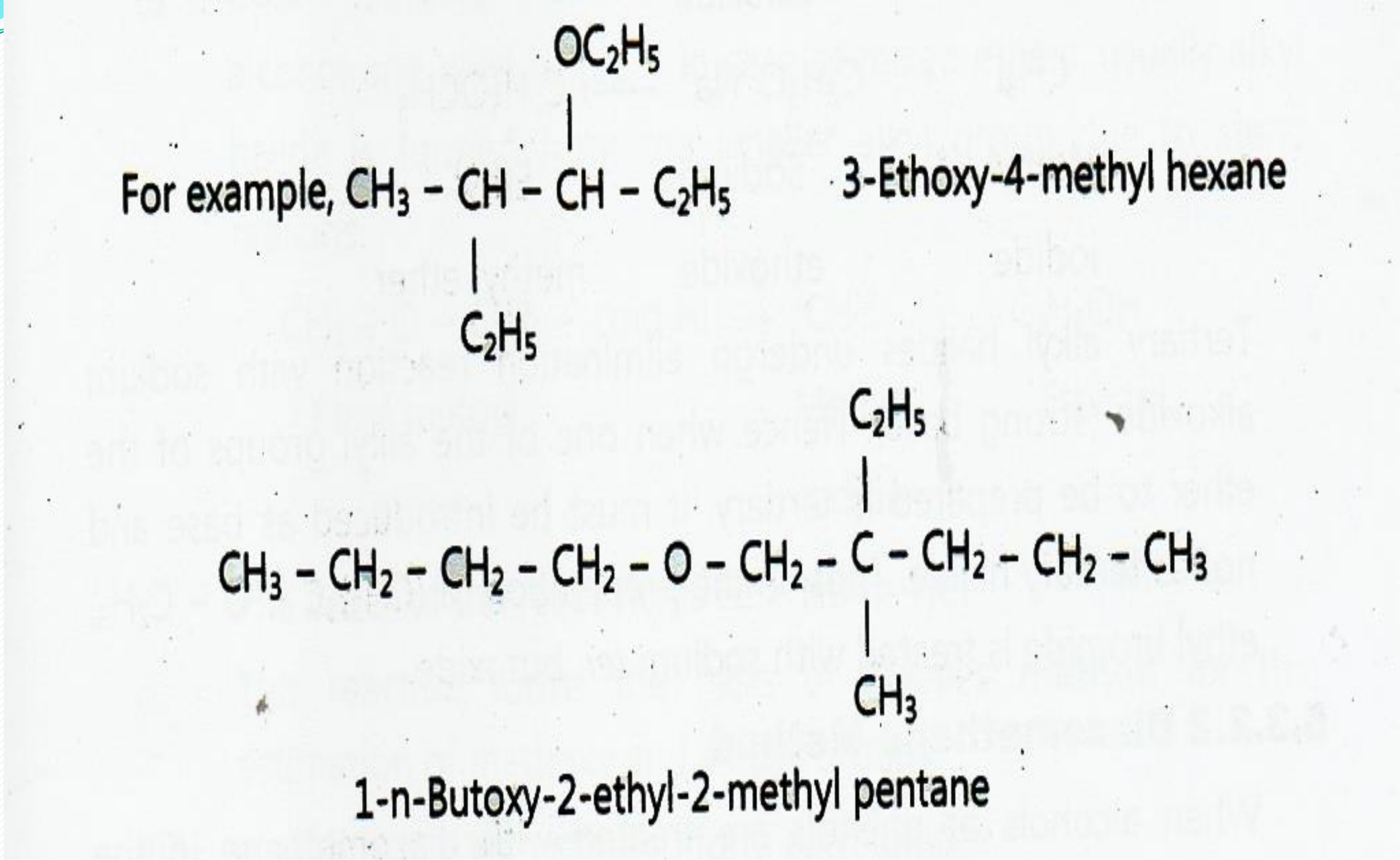
e.g. $CH_3 - O - C_2H_5$ (Ethyl methyl ether), $C_6H_5 - O - CH_3$ (Methyl phenyl ether).

Nomenclature



Nomenclature : The common names of ethers are derived from the two groups attached to the oxygen atom of the ether linkage. According to IUPAC system, ethers are named as 'alkoxy alkanes'.

Chemical Formula	Common Name	IUPAC Nomenclature
1. CH_3OCH_3	Dimethyl ether	Methoxymethane
2. $C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
3. $C_2H_5OCH_3$	Ethyl methyl ether	Methoxyethane
4. $C_6H_5OC_2H_5$	Phenyl ethyl ether	Ethoxybenzene
5. $C_3H_7OC_4H_9$	Butyl propyl ether	Propoxybutane
6. $C_6H_5OCH_3$	Anisole	Methoxybenzene
7. $(CH_3)_2CHOC_2H_5$	Ethyl isopropyl ether	Ethoxy-2-propane
8. $(CH_3)_2CHOC_4H_9$	n-Butyl isopropyl ether	1-Isopropoxybutane

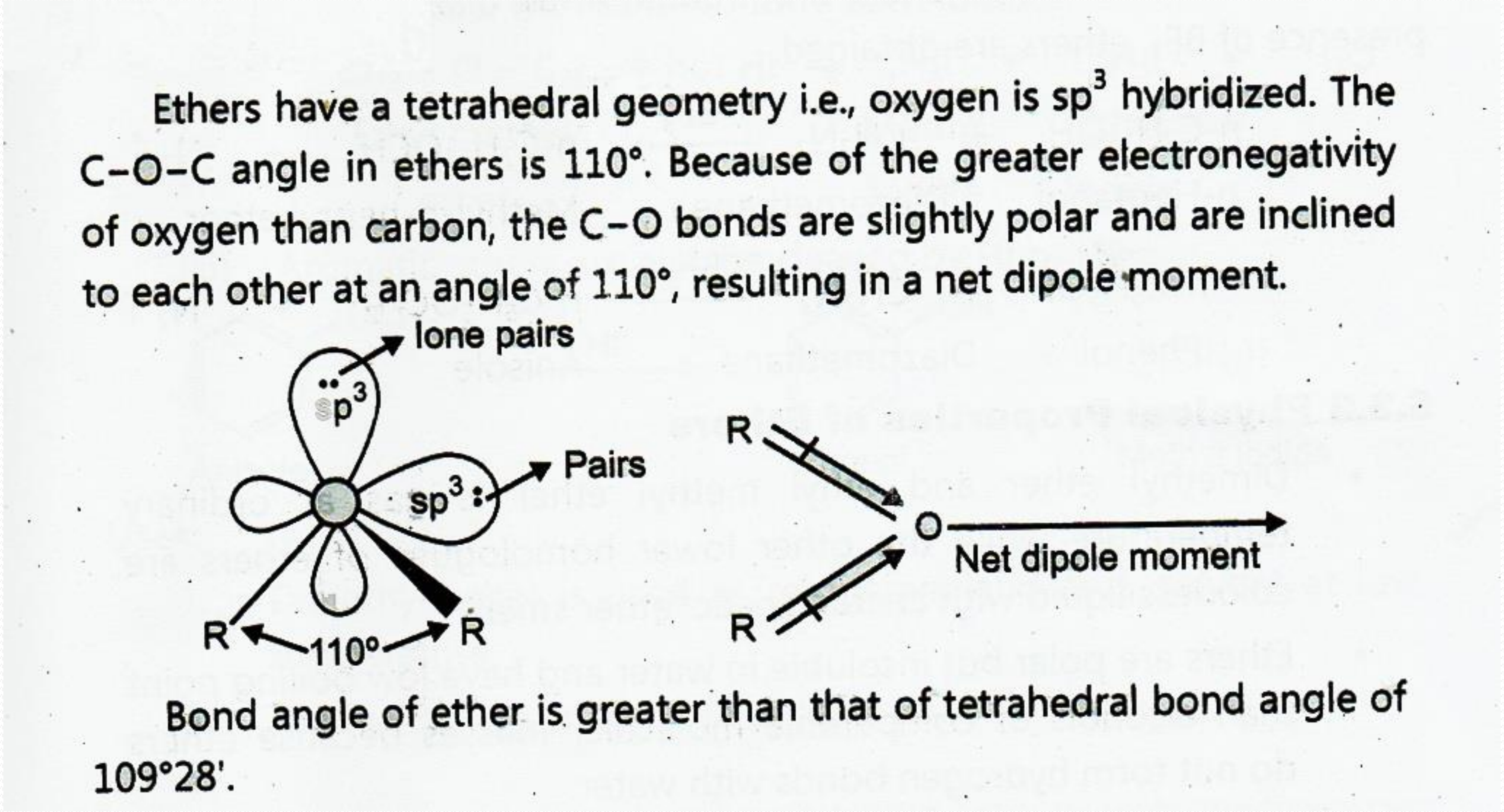


For example, $CH_3-\underset{\underset{C_2H_5}{|}}{CH}-\overset{\overset{OC_2H_5}{|}}{CH}-C_2H_5$ 3-Ethoxy-4-methyl hexane

$$CH_3-CH_2-CH_2-CH_2-O-CH_2-\overset{\overset{C_2H_5}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_2-CH_3$$

1-n-Butoxy-2-ethyl-2-methyl pentane

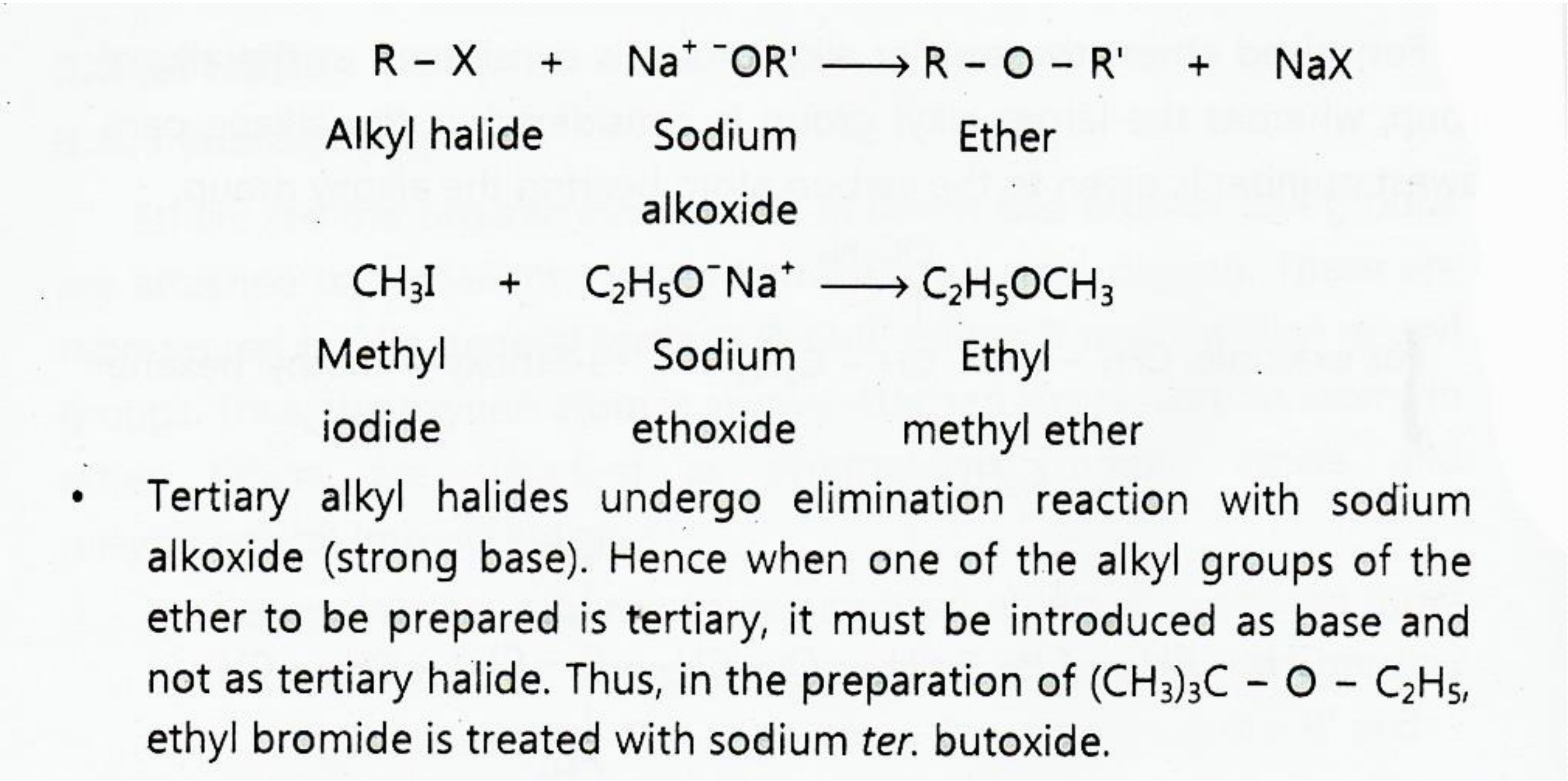
Structure of Ether



Ethers have a tetrahedral geometry i.e., oxygen is sp^3 hybridized. The C–O–C angle in ethers is 110°. Because of the greater electronegativity of oxygen than carbon, the C–O bonds are slightly polar and are inclined to each other at an angle of 110°, resulting in a net dipole moment.

Bond angle of ether is greater than that of tetrahedral bond angle of 109°28'.

Preparation of Ether
Williamson's Synthesis

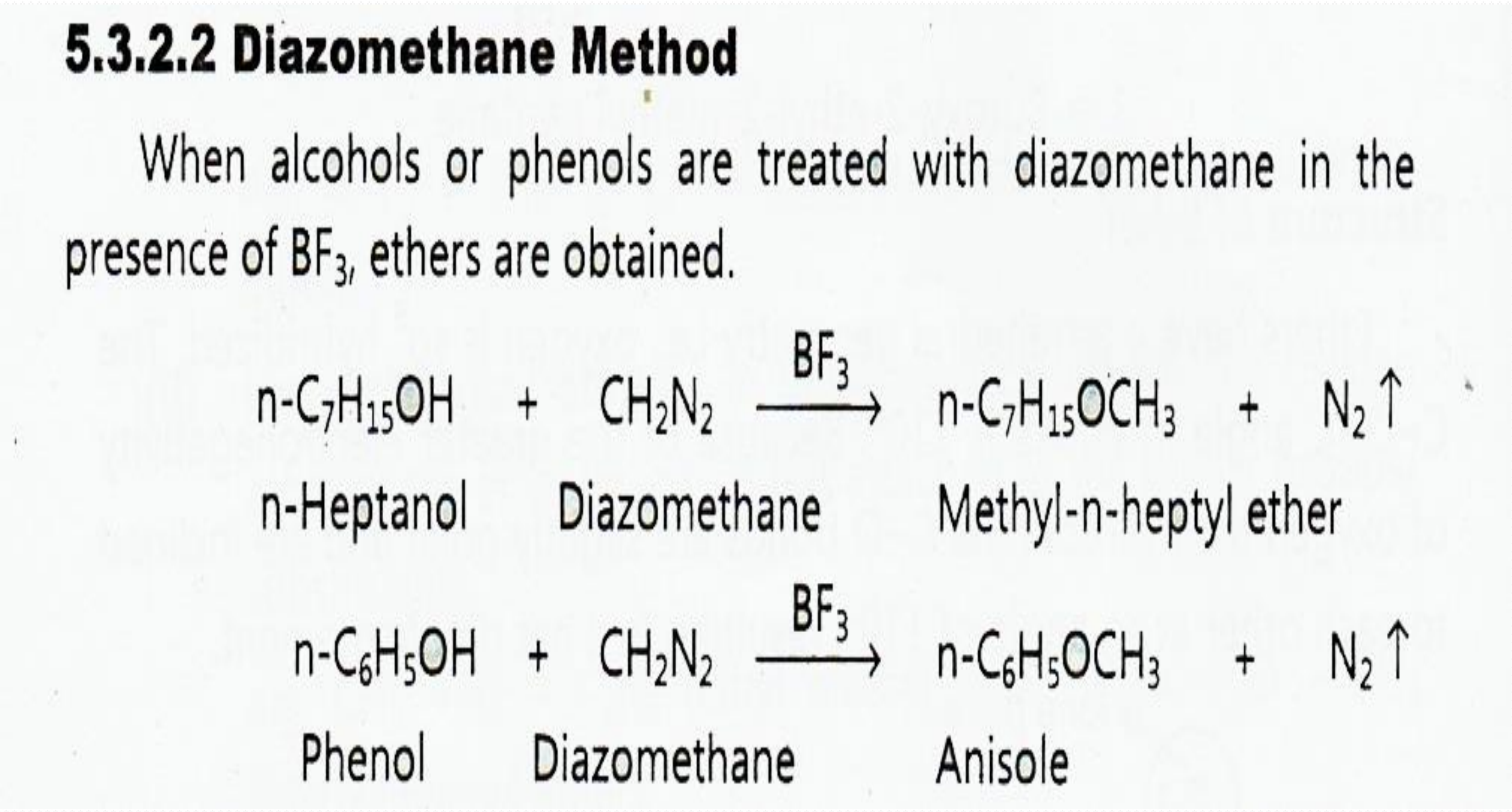


$$\underset{\text{Alkyl halide}}{R - X} + \underset{\text{Sodium alkoxide}}{Na^{+}\,{}^{-}OR'} \longrightarrow \underset{\text{Ether}}{R - O - R'} + NaX$$

$$\underset{\text{Methyl iodide}}{CH_3I} + \underset{\text{Sodium ethoxide}}{C_2H_5O^{-}Na^{+}} \longrightarrow \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3}$$

- Tertiary alkyl halides undergo elimination reaction with sodium alkoxide (strong base). Hence when one of the alkyl groups of the ether to be prepared is tertiary, it must be introduced as base and not as tertiary halide. Thus, in the preparation of $(CH_3)_3C - O - C_2H_5$, ethyl bromide is treated with sodium *ter.* butoxide.

Diazomethane Method



5.3.2.2 Diazomethane Method

When alcohols or phenols are treated with diazomethane in the presence of BF_3, ethers are obtained.

$$\text{n-}C_7H_{15}OH + CH_2N_2 \xrightarrow{BF_3} \text{n-}C_7H_{15}OCH_3 + N_2\uparrow$$

n-Heptanol Diazomethane Methyl-n-heptyl ether

$$\text{n-}C_6H_5OH + CH_2N_2 \xrightarrow{BF_3} \text{n-}C_6H_5OCH_3 + N_2\uparrow$$

Phenol Diazomethane Anisole

5.3.4 Reactions of Ethers

The ethers are highly stable towards the action of most of the chemical reagents. Thus, they are used as solvents in many reactions. However, if treated with strong acids like HI and HBr they hydrolyze to give alcohols or alkyl halides.

Reaction with halogen acids :

Ethers are readily cleaved by cold HI or HBr.

(i) Cold HI breaks the ether linkage and converts the ether to alcohol and alkyl halide. In case of mixed ethers, usually alkyl halide is formed from the smaller alkyl group due to steric reasons.

$$CH_3 - O - C_2H_5 + \text{cold HI} \rightarrow CH_3I + C_2H_5OH$$

Ethyl methyl ether — Methyl iodide — Ethanol

The order of the reactivity is HI > HBr > HCl.

This reaction forms the basis of **Zeisel's method** for the estimation of methoxy and alkoxy groups.

(ii) Hot HI reacts with ether to form alkyl iodides.

$$CH_3 - O - C_2H_5 + \text{hot HI} \rightarrow CH_3I + C_2H_5I + H_2O$$

Ethyl methyl ether — Methyl iodide — Ethyl iodide

(iii) Aromatic ethers are also be cleaved by HI or HBr.

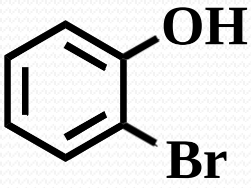
Anisole

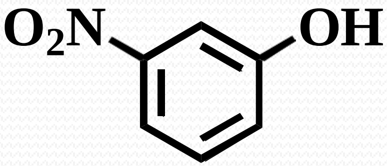
Phenol

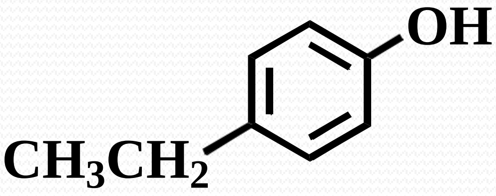
Methyl iodide

NOMENCLATURE OF PHENOLS

- The terms *ortho* (1,2-disubstituted), *meta* (1,3-disubstituted) and *para* (1,4-disubstituted) are often used in the common names.

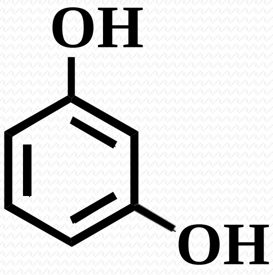




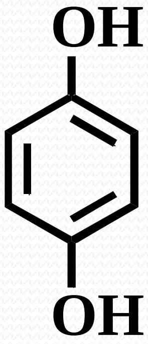


IUPAC name:	**2-bromophenol**	**3-nitrophenol**	**4-ethylphenol**
common name:	***ortho*-bromophenol**	***meta*-nitrophenol**	***para*-ethylphenol**

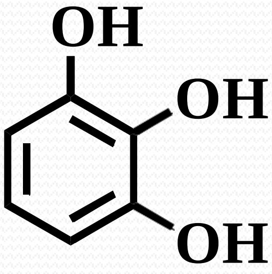
- **Phenols may be monohydric, dihydric or trihydric - (number of hydroxyl groups) in the benzene ring.**



benzene-1,3-diol



benzene-1,4-diol



benzene-1,2,3-triol