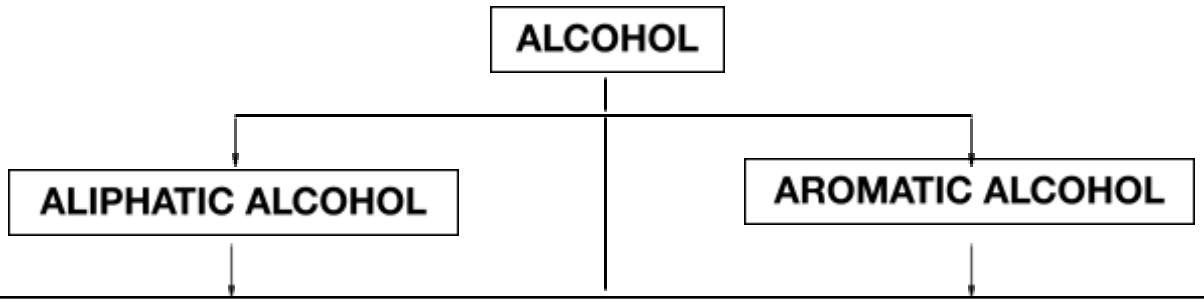
CHAPTER 8.0: HYDROXY COMPOUND

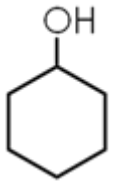
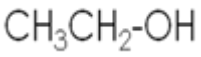
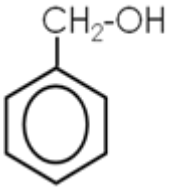
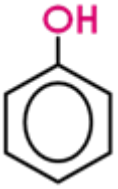
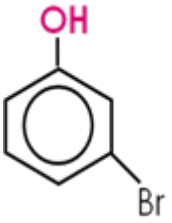
TOPIC	SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
			C1	C2	C3	C4
Hydroxy Compounds	8.1 Nomenclature	a) Draw the structures, classify and name the hydroxy compounds (parent chain ≤C_{10}) according to IUPAC nomenclature		√		
	8.2 Physical properties of Alcohols	a) Analyze the physical properties: i. Boiling point ii. Solubility in water				√
	8.3 Preparation of Alcohols	a) Explain the preparation of alcohol by: i. Fermentation ii. Hydration of alkenes iii. Hydrolysis of haloalkanes iv. Addition of Grignard reagents to carbonyl compounds			√	
		b) Outline the synthesis of alcohols			√	
	8.4 Chemical properties of Alcohols	a) Explain the reactions of alcohols with reference to: i. Reaction with sodium ii. Esterification iii. Dehydration iv. Substitution reactions using HX, PX_3, PCl_5 or $SOCl_2$			√	
		b) Explain the oxidation reactions with $KMnO_4/H^+$, $Cr_2O_7^{2-}/H^+$, CrO_3/H^+ and PCC/CH_2Cl_2			√	
		c) Explain the identification tests to distinguish classes of alcohols using Lucas reagent, i.e. concentrated $HCl/ZnCl_2$				√
		d) Outline the synthesis of compounds related to reactions of alcohols				√
		e) Explain iodoform test, i.e I_2/OH^- to identify methyl carbinol $CH_3CH(OH)$			√	
	8.5 Phenol	a) Compare the acidity of phenol, alcohol and water				√
		b) Explain the chemical properties of phenol with reference to: i. Reaction with sodium ii. Reaction with sodium hydroxide iii. Identification tests using $FeCl_3$ solution and bromine water			√	

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
8.1 Nomenclature	a) Draw the structures, classify and name the hydroxy compounds (parent chain ≤C_{10}) according to IUPAC nomenclature		√		

INTRODUCTION

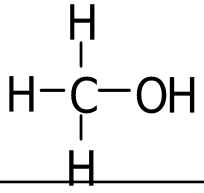
Functional group ⇒ Hydroxyl (–OH)

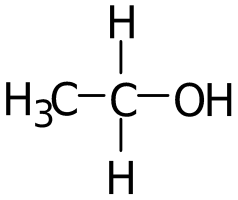
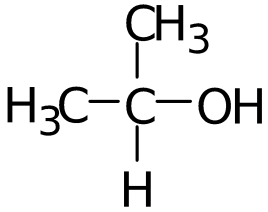
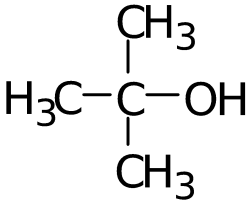


▯ Organic compound with at least one **hydroxyl group (–OH) attach to alkyl group.** ▯ General formula : **$C_nH_{2n+1}OH$** Example:   	▯ Organic compounds that contain a **hydroxyl group (-OH) bonded directly to a carbon atom of the benzene ring.** Example:  

CLASSIFICATION OF ALCOHOL

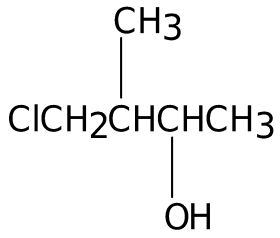
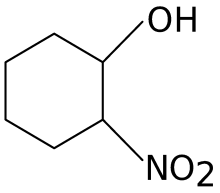
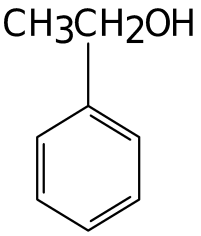
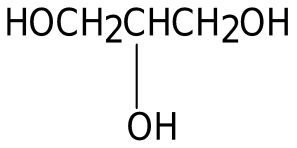
▯ Alcohol are classified based on the **carbon atom** to which the **hydroxyl group** is directly attached.

Classification	General Formula	Explanation
Methyl alcohol		**Hydroxyl group bonded to methyl group.**

Primary alcohol (1°)		**Hydroxyl group bonded to 1° carbon atom.**
Secondary alcohol (2°)		**Hydroxyl group bonded to 2° carbon atom.**
Tertiary alcohol (3°)		**Hydroxyl group bonded to 3° carbon atom.**

IUPAC NOMENCLATURE OF ALIPHATIC ALCOHOL	
Step 1:	**Identify** and **determines the parent name** for alcohol Rule 1: Choose the **longest carbon chain containing –OH group**. Rule 2: The suffix **'–e'** in the **alkane** parent name is **replaced by '–ol'**

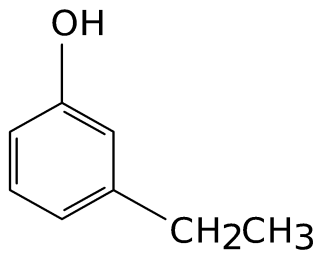
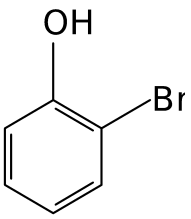
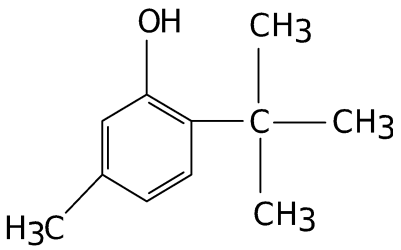
Step 2:	**Number the longest continuous chain** Rule 1: Number the carbon atoms in the longest chain so that the carbon atom attached to **–OH group** is given the **lowest possible number.** Rule 2: The **position of the hydroxyl group** is indicated by the number of the carbon atom to which it is attached.
Step 3:	**Give the IUPAC nomenclature for alcohol** Rule 1: Name all the substituent present in the alcohol molecule and give their numbers. Rule 2: Alcohol with two **–OH groups** are called **diols** and those **three –OH groups** are called **triols.**

Example:		
		
$H_2C{=}CHCH_2OH$	$HOCH_2CH_2OH$	

Alcohol with 2 hydroxy groups

Structure	IUPAC name	General name
$CH_2(OH)CH_2OH$	1,2–ethanediol	Ethylene glycol
$CH_3CH(OH)CH_2OH$	1,2–propanediol	Propylene glycol
$HOCH_2CH_2CH_2OH$	1,3–propanediol	Trimethyl glycol
$HOCH_2CH(OH)CH_2OH$	1,2,3–propanetriol	Glycerol

IUPAC NOMENCLATURE OF PHENOL

Exercises:

Write the structural formulae of the following alcohols and classify them as primary, secondary or tertiary alcohols.

1. 2–methyl–1–propanol	2. 2–phenyl–2–butanol
3. 4–penten–2–ol	4. 3–methylhexanol

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
8.2 Physical properties of alcohols	a) Analyze the physical properties: i. Boiling point ii. Solubility in water				√

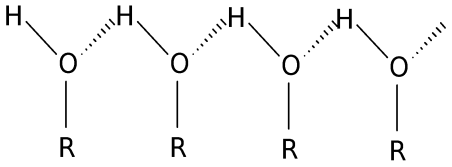
PHYSICAL PROPERTIES OF ALCOHOL

PHYSICAL PROPERTIES OF ALCOHOL

- BOILING POINT
- SOLUBILITY IN WATER
- ACIDITY

[redacted]

- The **high electronegativity difference** between **O and H** makes alcohol molecules **highly polar.**
- Alcohol molecules are attracted to each other by **hydrogen bond**



- Higher energy is needed to separate the molecules.

Factors affecting boiling point:

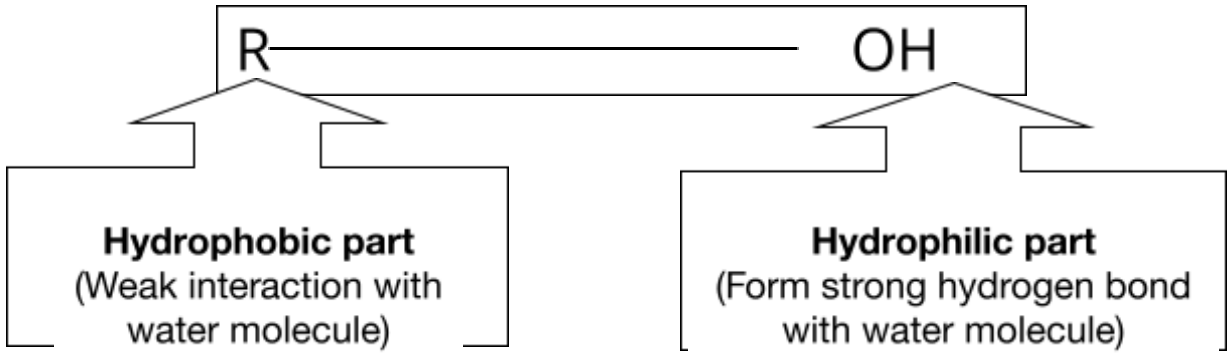
- Molecular weight
- Number of –OH group
- Number of branched (isomeric alcohol)

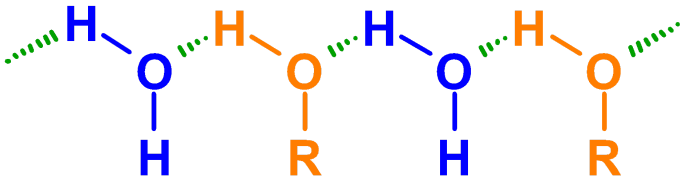
Molecular weight increases, total surface area increase, **BP increases** due to the	**Number of –OH group** increases, BP increases due to the **increase in**	**Straight chain** has a **bigger contact area** compared to branched alcohol, hence,

increase in strength of Van Der Waals Forces. ▯ **BP** of **R-OH** is higher than the corresponding **hydrocarbon** due to the **ability of alcohol to form hydrogen bond.**	**the number of hydrogen bond**	**stronger Van der Waals** forces, higher BP. ▯ **BP straight chain alcohol >branched chain alcohol** ▯ 1° > 2° > 3°

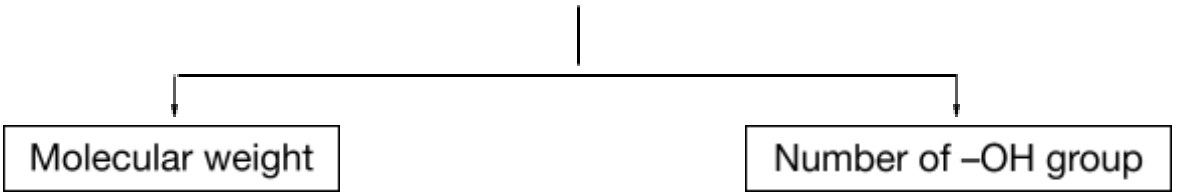
[redacted]

- Lower alcohols **(≤ 5C)** – **completely soluble in water**.
- Longer C chain (>5C) – **insoluble in water**.
- Alcohols and water ⟶ presence **–OH group** in the molecules.
- Therefore, they have the **ability to form intermolecular hydrogen bonding**.
- **–OH** group gives alcohol a **hydrophilic character.**





Factors affecting solubility:



As the **molecular weight increases**, the **hydrophobic area (R group)** becomes **larger.** ⇒ **water solubility decreases.**	When number of **–OH groups increases,** the **solubility in water also increases.** ⇒ due to **ability to form more hydrogen bonds** with **water molecule increases.**

Exercises:

1. Arrange the compound below in ascending order of boiling point.

Organic compound	Molar mass (g/mol)
$CH_3CH_2CH_2CH_2OH$	74
$CH_2OHCH_2CH_2OH$	76
$CH_3CH_2CH_2Cl$	79.5
$CH_3CH_2CH_2CH_2CH_3$	72

2. Arrange the following compound in increasing order of boiling point. Explain.

1,2-ethanediol,n-butane,1-propanol,1,3-propanediol

Answer:

General explanation:

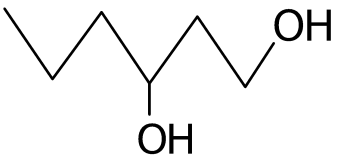
- **Boiling point increase** with the increase in the **number of hydrogen bond** and the **increase in the strength of Van Der Waals forces**.
- **Van Der Waals forces increase** with the **increase in molecular weight**.
- **Hydrogen bond** is **stronger than** Van Der Waals forces.

Specific:

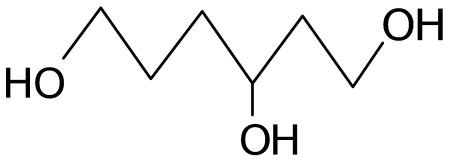
- …….. and …….. have …….. OH group, hence can form same number of hydrogen bond but …… has higher molecular weight compared to ……
  So, it has stronger Van Der Waals forces, hence has the highest boiling point.
- …….. .. has only one –OH group, fewer number of hydrogen bond.
- ……. the lowest boiling point because cannot form hydrogen bond and only weak Van Der Waals force exist between its molecules.

3. Arrange the compounds in decreasing order of solubility in water.

A



B



C

Answer:

4. Arrange the compounds in each set in decreasing order of solubility in water. Explain.

hexane, 1–hexanol, 1,2–ethanediol

Answer:

Explanation:

- ..... is the most soluble because it has ..... OH groups, therefore it can form .....hydrogen bond with water molecule compared to ..... that has only ..... OH group.
- Whereas, ... does not has any OH group present in the compound and it ..... form hydrogen bond with water molecule. Therefore, it is ..... in water.

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
8.3 Preparation of Alcohols	a) Explain the preparation of alcohol by: i. Fermentation ii. Hydration of alkenes iii. Hydrolysis of haloalkanes iv. Addition of Grignard reagents to carbonyl compounds			√	
	b) Outline the synthesis of alcohols			√	

PREPARATION OF ALCOHOL

[redacted]

- Fermentation of Sugar
- Hydrolysis of Haloalkanes
- Hydration of Alkenes
- Addition of Grignard Reagents to Carbonyl Compounds

[redacted]

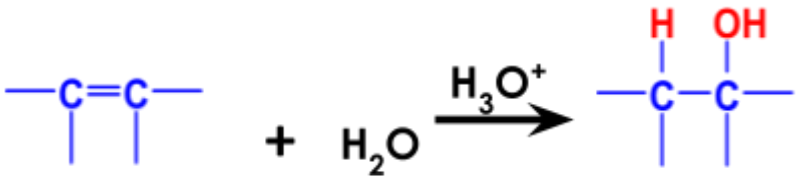
- This method applies **only** to **ethanol** and **NOT** any other alcohol this way.
- The reaction is **catalyzed** by the enzymes in yeast.

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

[redacted]

- Alkenes was added to H_2O and H_2SO_4 as a catalyst.
- Reagent: H_2O, H_3O^+
- Addition of water to an alkene follows Markovnikov's Rule

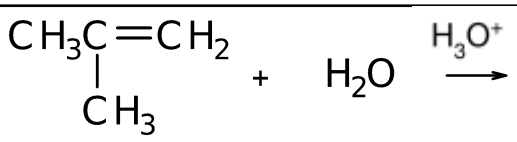
General:



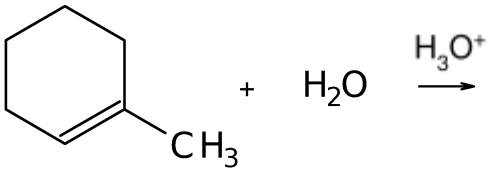
alkene alcohol

Example:

i.



ii.



[redacted]

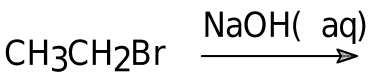
- Reagent: NaOH(aq)

General:

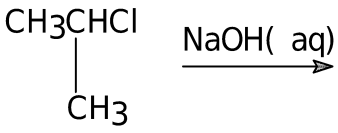
⇒ 1° haloalkane will form 1° alcohol
⇒ 2° haloalkane will form 2° alcohol
⇒ 3° haloalkane will form 3° alcohol

Example:

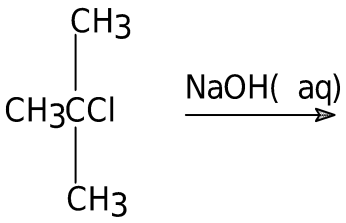
i.



ii.

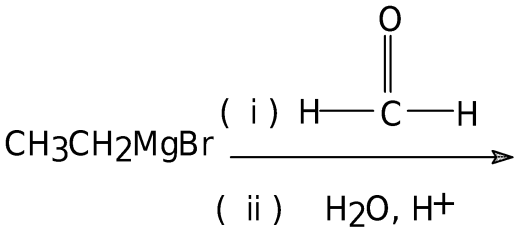


iii.

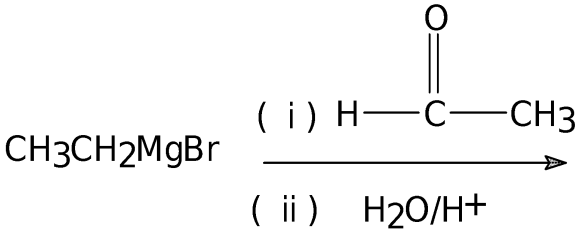


- **1°, 2° and 3° alcohol** can be prepared by the addition of **Grignard reagent with carbonyl compounds followed by hydrolysis.**

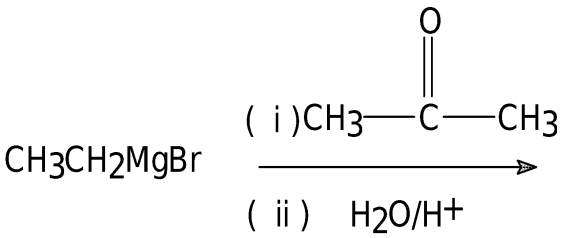
Synthesis of 1°alcohol ⇒ Grignard Reagent + methanal



Synthesis of 2°alcohol ⇒ Grignard Reagent + aldehyde



Synthesis of 3°alcohol ⇒ Grignard Reagent + ketone



Exercise:

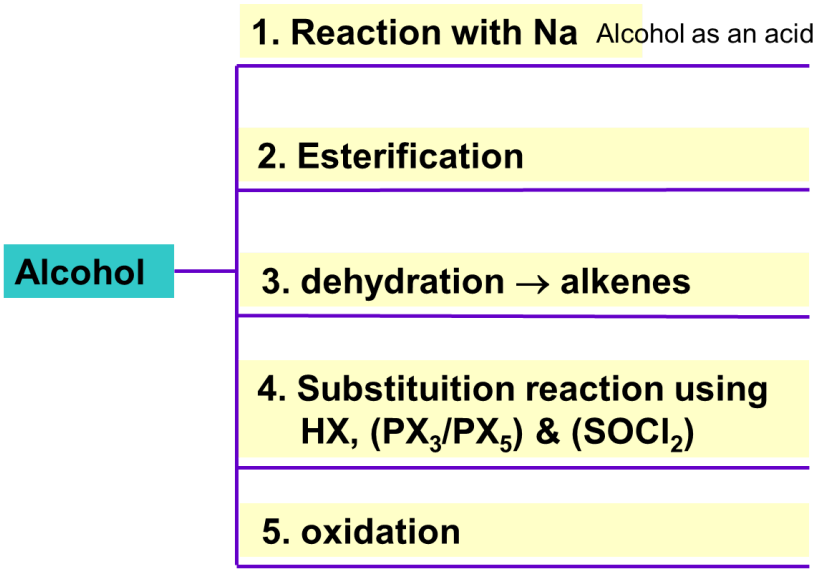
Write the chemical equation for the following reaction:

a) tert-butyl alcohol from an alkene

b) isopropyl alcohol from an alkyl halide

SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
8.4 Chemical Properties of alcohol	a) Explain the reactions of alcohols with reference to: i. Reaction with sodium ii. Esterification iii. Dehydration v. Substitution reactions using HX, PX_3, PCl_5 or $SOCl_2$			√	
	b) Explain the oxidation reactions with $KMnO_4/H^+$, $Cr_2O_7^{2-}/H^+$, CrO_3/H^+ and PCC/CH_2Cl_2			√	
	c) Explain the identification tests to distinguish classes of alcohols using Lucas reagent, i.e. concentrated $HCl/ZnCl_2$				√
	d) Outline the synthesis of compounds related to reactions of alcohols				√
	e) Explain iodoform test, i.e I_2/OH^- to identify methyl carbinol $CH_3CH(OH)$			√	

CHEMICAL PROPERTIES OF ALCOHOL



Reaction of Alcohols

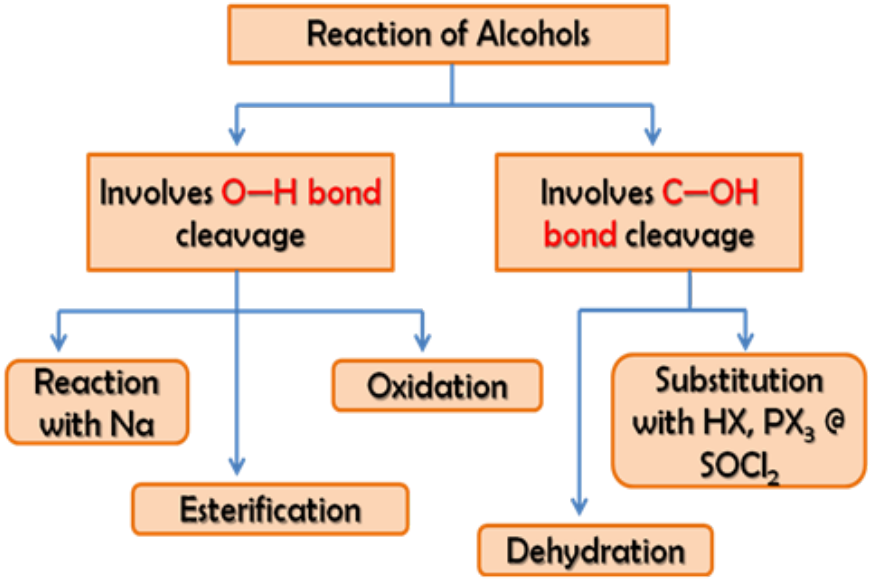
- involves two types of bond cleavage:

1) O—H Bond Cleavage
   Alcohol act as a weak acid (proton donor).

$$R\text{-}O\text{-}H + H_2O \rightarrow R\text{-}O^- + H_3O^+$$

2) C—OH Bond Cleavage
   Alcohol act as bases (electron pair donor).

$$R\text{-}OH + HA \rightarrow R\text{-}A + H_2O$$



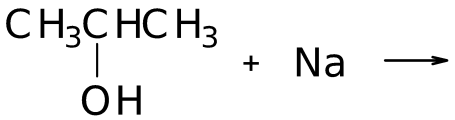
[redacted]

- In an aqueous solution, alcohol reacts as a **very weak acid.**
- **Alcohol reacts with Na** to form **sodium alkoxide** and **hydrogen gas.**
- General: $ROH + Na \rightarrow RO^-Na^+ + \frac{1}{2}H_2$

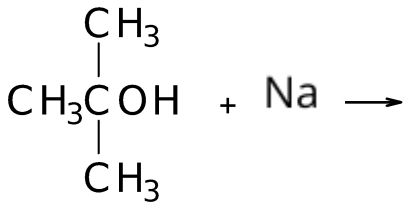
Example:

i. $CH_3CH_2OH + Na \rightarrow$

ii.



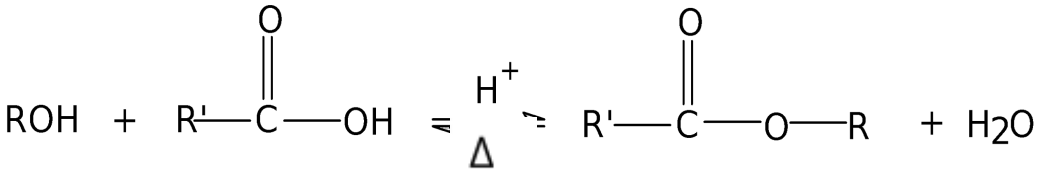
iii.



[redacted]

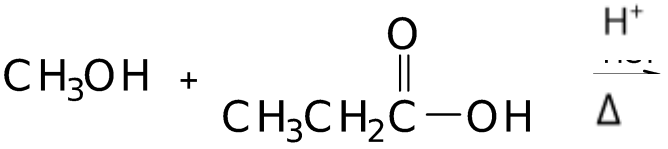
- Alcohol reacts with **carboxylic acid** under **reflux** & is **catalysed** by mineral acids conc H_2SO_4 or gaseous HCl to produce **ester.**

- **Reagent : H^+, Δ**

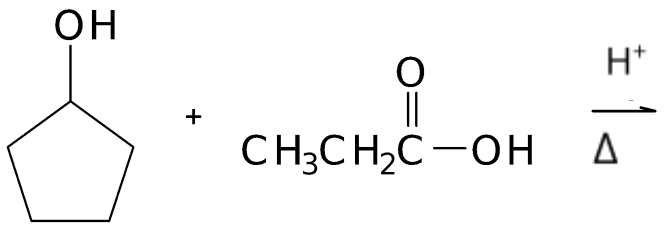


Example:

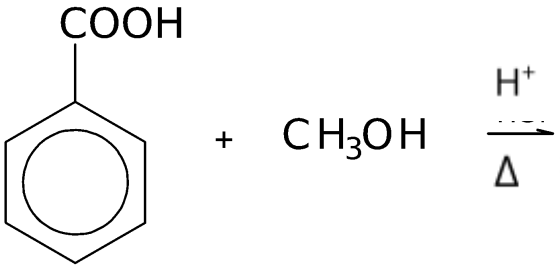
i.



ii.

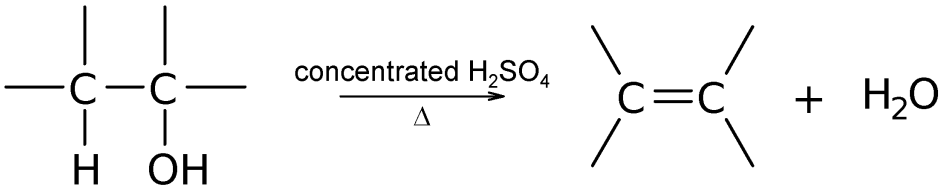


iii.



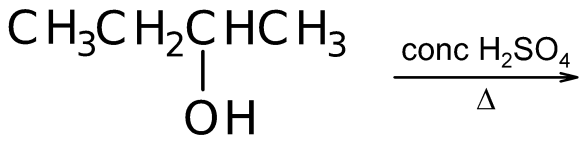
[redacted]

- **Rule** : **Saytzeff's Rule –** use to determine **major product**
- Involve **formation of alkene**
- **Possible rearrangement of carbocation** to get major
- **Reagent** : **conc.H_2SO_4, Δ**
- General:

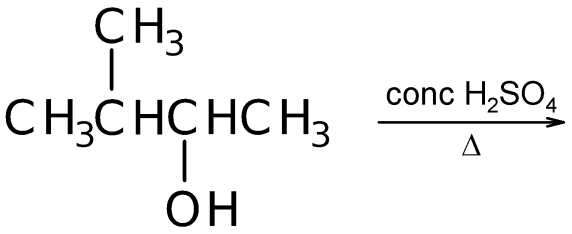


Example:

i.



ii.



[redacted]

Alcohol

- Alcohols react with a variety of reagents to produce **alkyl halides.**
- The most common reagents are:
  - Hydrogen halides, **HX**
  - Phosphorus trihalides, **PX_3**
  - Phosphorus pentahalides, **PX_5**
  - Thionyl chloride, **$SOCl_2$**

Reaction with hydrogen halides (HCl, HBr or HI)

- General reactions:

$$ROH + HX \longrightarrow RX + H_2O$$

- **Reaction with phosphorus trihalides (PBr_3 or PCl_3)**

- General reactions:

$$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$$

- **Reaction with phosphorus pentahalides (PBr_5 or PCl_5)**

- General reactions:

$$ROH + PX_5 \longrightarrow RX + HX + POX_3$$

- **Reaction with thionyl chloride ($SOCl_2$)**

- General reactions:

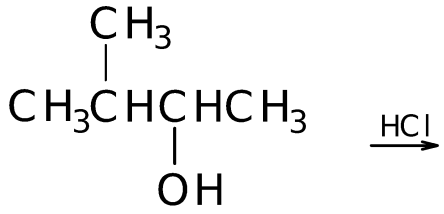
$$ROH + SOCl_2 \xrightarrow{\text{pyridine}} RCl + HCl + SO_2$$

Example:

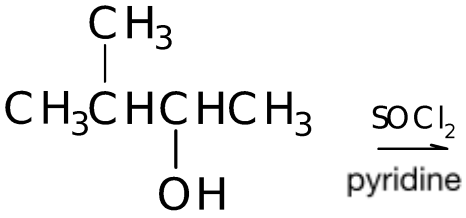
i.

$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow{HBr}$$

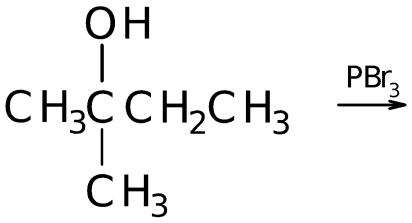
ii.


CH3
CH3CHCHCH3
OH
HCl

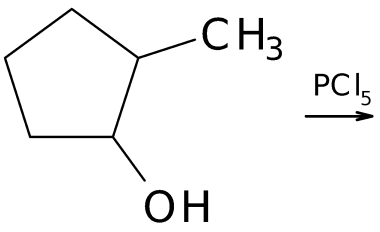
iii.


CH3
CH3CHCHCH3
OH
SOCl2
pyridine

iv.

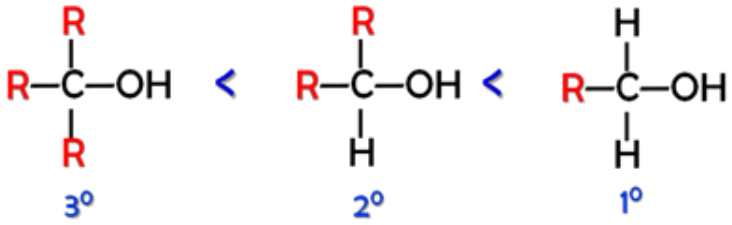

OH
CH3C CH2CH3
CH3
PBr3

v.


CH3
OH
PCl5

- **Oxidation product** depends on the **class of alcohol** used.

- The order of reactivity towards oxidation reaction:



- **Strong oxidising agent:**
  - Potassium permanganate, **$KMnO_4$**
  - Potassium dichromate, **$K_2Cr_2O_7$**
  - Sodium dichromate, **$Na_2Cr_2O_7$**
  - Chromic acid, **H_2CrO_4**
  - Chromium trioxide, **CrO_3/H^+**

OXIDATION PRODUCT : **CARBOXYLIC ACID**

- **Weak oxidising agent:**
  - Pyridinium chlorochromate in dichloromethane, **PCC in CH_2Cl_2**

OXIDATION PRODUCT : **CARBONYL**

Class of alcohol	Reaction with	Product
1°	**$KMnO_4/K_2Cr_2O_7@Na_2Cr_2O_7$ (strong)**	**Carboxylic acid**
	PCC, CH_2Cl_2 (weak)	**aldehyde**
2°	**$KMnO_4/K_2Cr_2O_7@Na_2Cr_2O_7$ (strong)**	**ketone**
3°	**$KMnO_4/K_2Cr_2O_7@Na_2Cr_2O_7$ (strong)**	**Does no undergo oxidation**

Example:

i.

$$CH_3CH_2OH \xrightarrow{KMnO_4,\ H^+,\ \Delta}$$

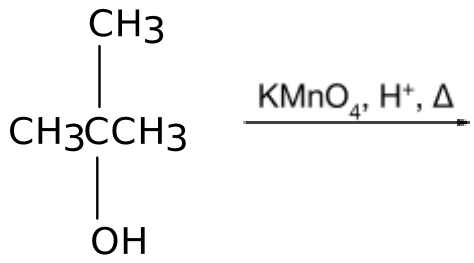
ii.

$$CH_3CH_2OH \xrightarrow{PCC,\ CH_2Cl_2}$$

iii.

$$CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3 \xrightarrow{Na_2Cr_2O_7,\ H^+,\ \Delta}$$

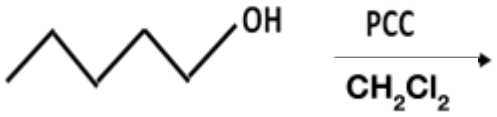
iv.



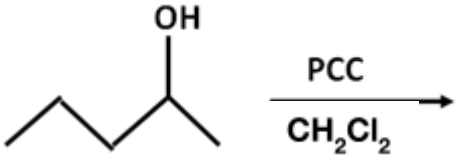
Exercise

1. Draw the organic products in each of the following reactions?

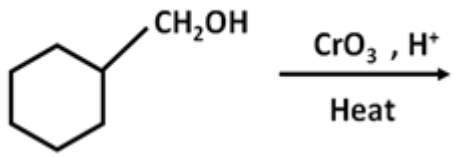
a)



b)



c)



2. Outline the method of preparation for each of the following compounds using the **ethanol** as the starting material.

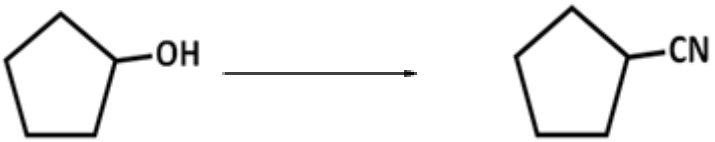
   a) Propanoic acid

   b) 1,2–dibromoethane

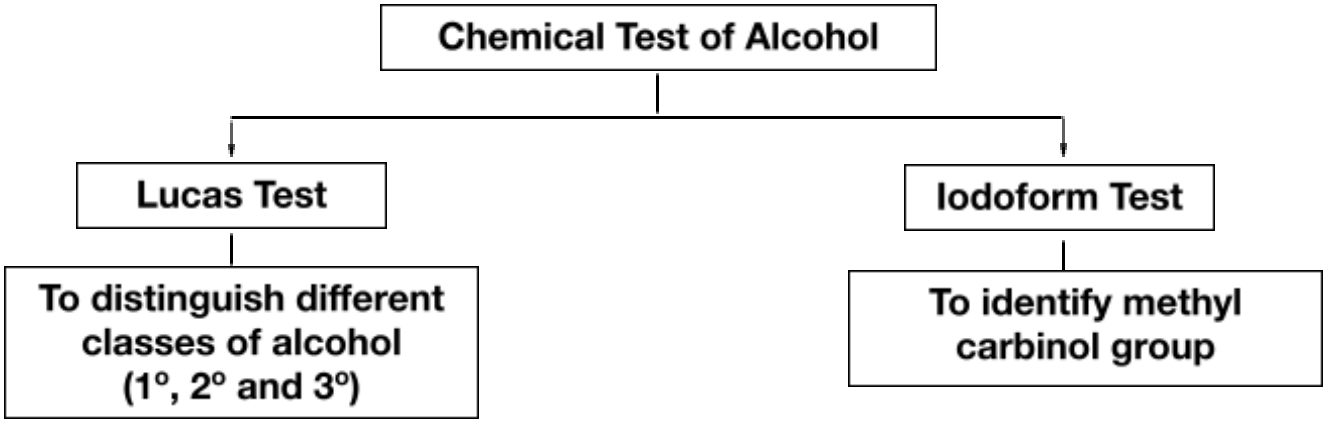
3. Prepare each compound from cyclopentanol. In some cases, more than one step is needed.

a)

b)

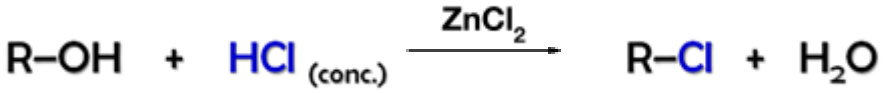


IDENTIFICATION TEST (CHEMICAL TEST FOR ALCOHOL)



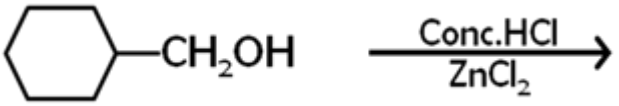
Lucas Test

- Used to differentiate 1°, 2° and 3° alcohols by observing the **rate of reaction** between **alcohols and Lucas reagent** to form alkyl chlorides.
- Reagent : **HCl(conc), $ZnCl_2$**
- General reaction:

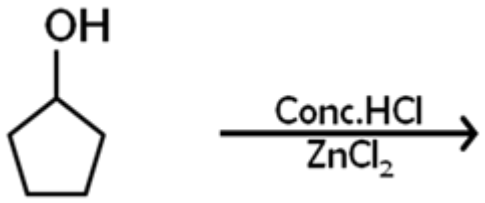


Class of alcohol	Observation
Primary (1°)	Solution does not turn cloudy even after 10 minutes of heating
Secondary (2°)	Solution turns cloudy within 5 – 10 minutes
Tertiary (3°)	Cloudy solution appears immediately
Phenol	Does not react with Lucas reagent even through heating

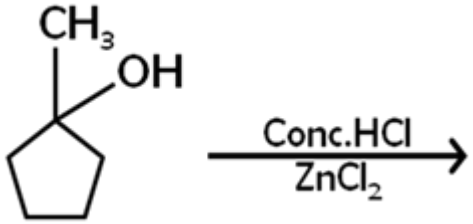
Example:

i. 

Observation:

ii. 

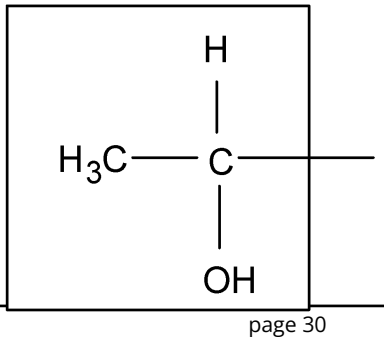
Observation:

iii. 

Observation:

Iodoform Test

- To identify the presence of **methyl alcohol** group **(*methyl group attached to OH carbon atom)**
- **Reagent : I_2 in $NaOH_{(aq)}$**

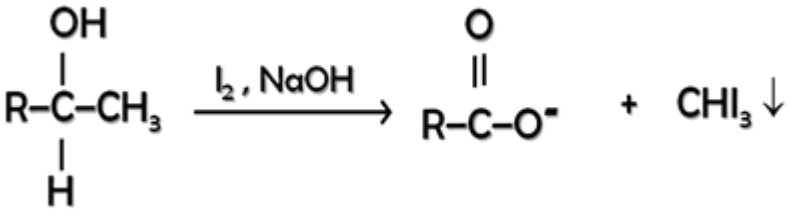


methyl carbinol group

- **Observation : Yellow precipitate formed.**

- Methyl carbinol group cleavage to form **carboxylate ion** and **haloform**.

- General reaction:

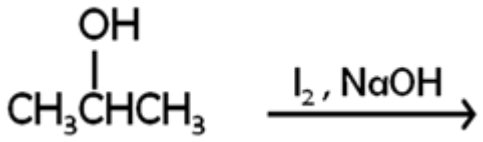


- **Observation : Yellow precipitate formed.**

Exercise:

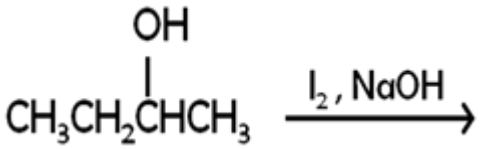
1. Which of the following alcohol give positive iodoform test?

i.



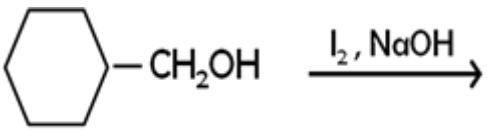
Observation:

ii.



Observation:

iii.



Observation:

2. Suggest chemical test to differentiate the following pairs of compounds. State the reagents, observation and write chemical equation involved.

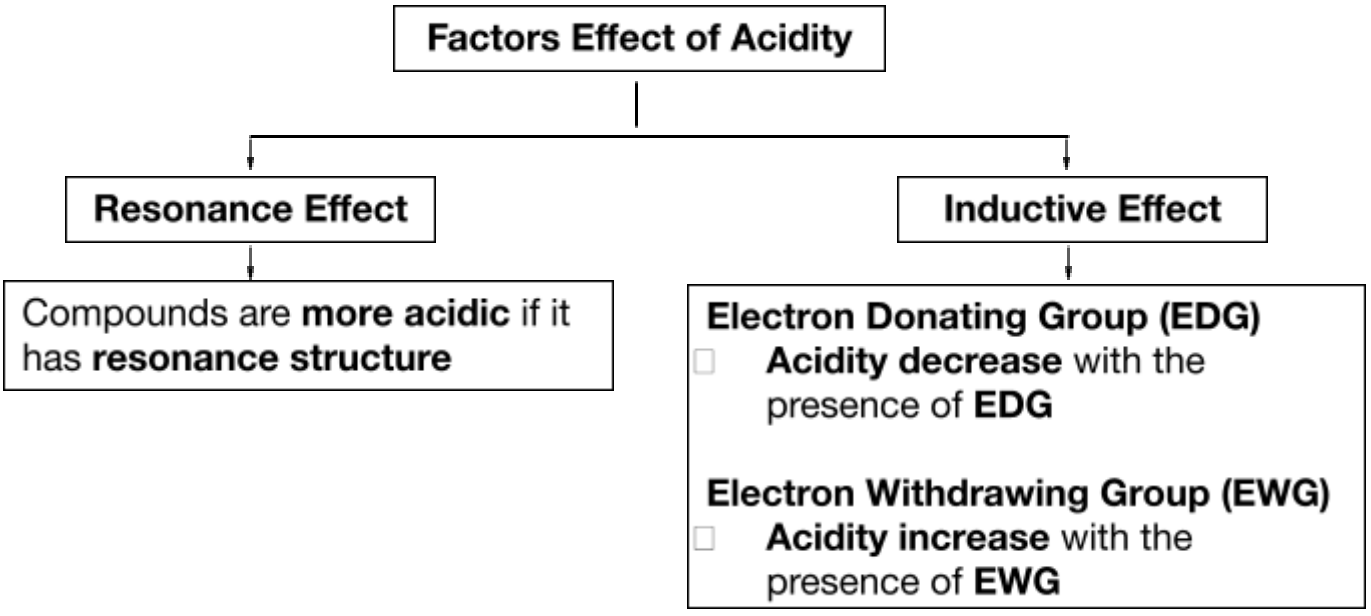
   a) 2-methyl-1-propanol from 2-methyl-2-propanol

   b) Benzene and cyclohexanol

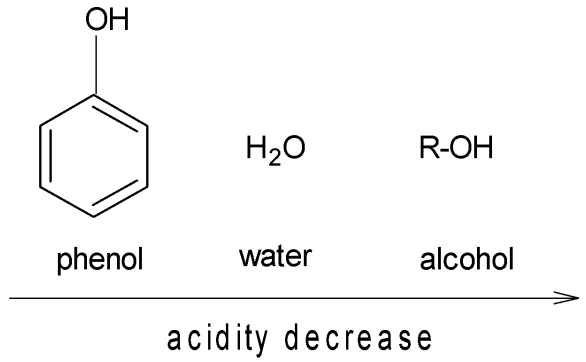
SUBTOPIC	LEARNING OUTCOMES	MAPPING COGNITIVE DOMAINS			
		C1	C2	C3	C4
8.5 Phenol	a) Compare the acidity of phenol, alcohol and water				√
	b) Explain the chemical properties of phenol with reference to: i. Reaction with sodium ii. Reaction with sodium hydroxide iii. Identification tests using $FeCl_3$ solution and bromine water			√	

PHENOL

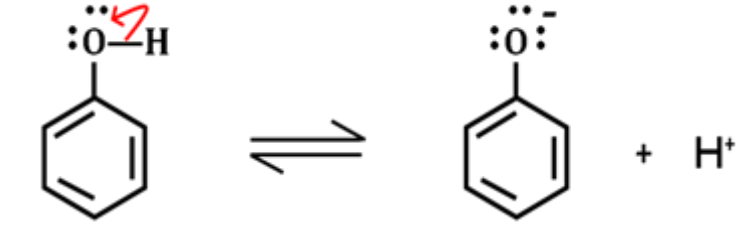
- **Alcohols, water and phenol** act as **acids** by **donating proton** (O−H cleavage)
- Anything that **stabilizes the conjugate base** makes the acid **more acidic**.
- The **higher the stability of the conjugate base the higher the acidity**.



Comparison acidity:



Phenol dissociates to form **phenoxide** and **hydrogen ion**.



Phenol **Phenoxide ion**

- Phenol is the **most acidic** because the **phenoxide ion is stable**.
- The acidity of phenol is due to the **negative charge on oxygen atom** can be **delocalized onto the benzene ring** (stabilized by **resonance effect**)

Alcohol is less acidic compared to water.

Alcohol: $R—OH \rightleftharpoons RO^- + H^+$

alcohol — alkoxide ion

Water: $H_2O \rightleftharpoons HO^- + H^+$

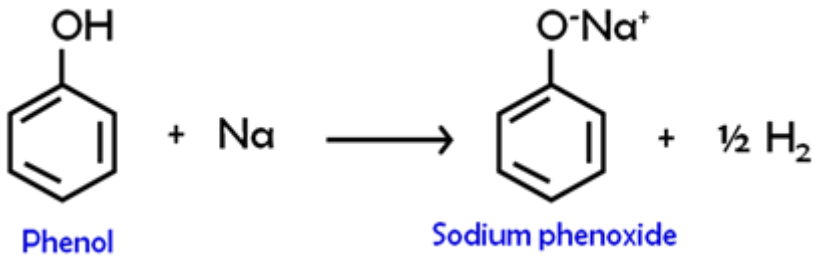
water — hydroxide ion

- The presence of **alkyl group (electron donating group, EDG)** on alkoxide ion **increase the density of negative charge on the oxygen atom**.
- This makes the **alkoxide ion less stable** compared to **hydroxide ion.**

CHEMICAL PROPERTIES OF PHENOL

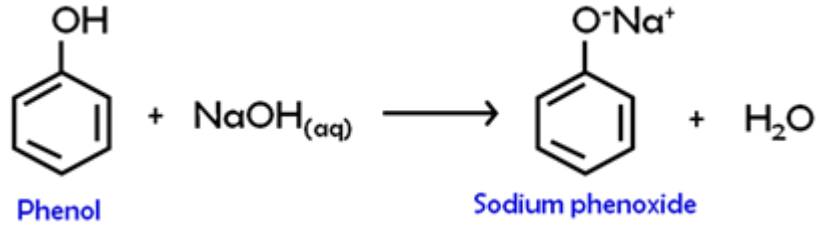
[redacted]

- When sodium is added to a solution of phenol at room temperature, H_2 gas is liberated.
- **Reagent: Na**



[redacted]

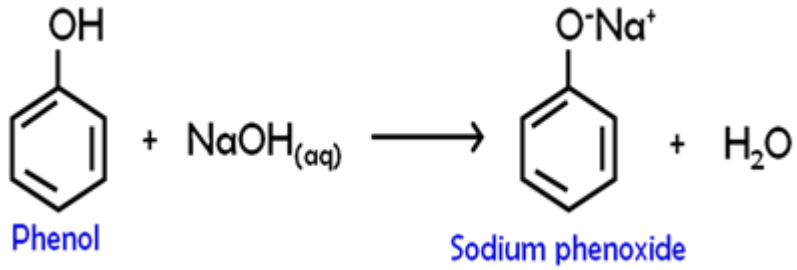
- Phenol is **slightly soluble in water** but **dissolve in aqueous solution of NaOH** at room temperature to produce **sodium phenoxide and water**.
- **Reagent: NaOH**

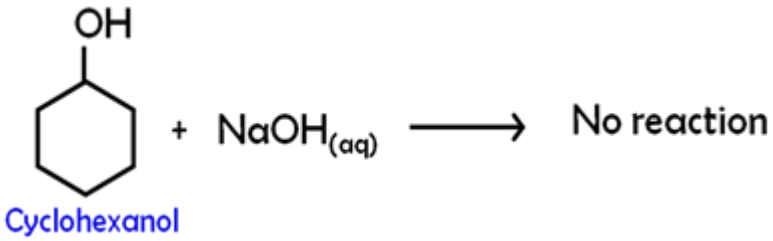


TAKE NOTE!

The reaction with NaOH is often used as a **chemical test** to **differentiate aliphatic alcohol and phenol!**

Example:

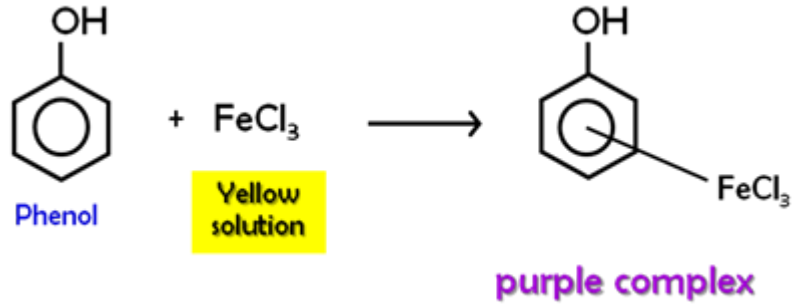




IDENTIFICATION TEST OF PHENOL

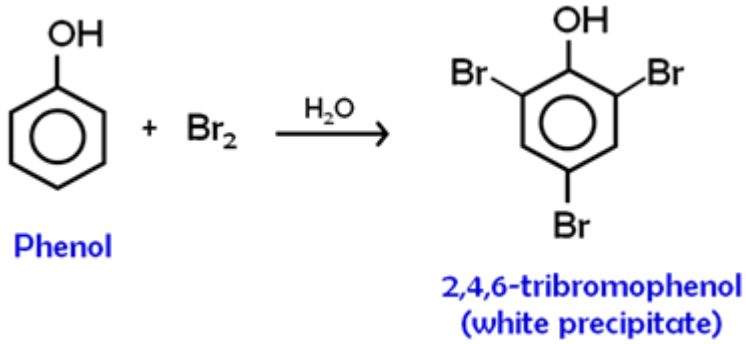
[redacted] ⇒ **used to differentiate phenol from other compound**

- Reagent : **$FeCl_3$ solution**
- Condition : **At room temperature**
- Observation : **Formation of purple complex**



[redacted] ⇒ **used to differentiate phenol from other compound**

- Reagent : **Br_2 in H_2O**
- Condition : **At room temperature**
- Observation : **Reddish brown colour of bromine decolourised and white precipitate formed.**



Exercise:

Suggest a chemical test to differentiate the following pairs of compounds

a) Phenol from benzyl alcohol

b) 1,2-ethanediol and phenol