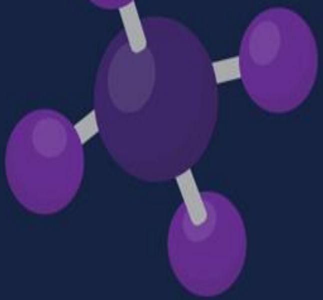


Chapter 8

HYDROXY COMPOUNDS

8.2 Physical Properties

8.1 Introduction

8.3 Preparation

8.0 HYDROXY COMPOUNDS

8.4 Chemical Properties

8.5 Phenol

8.1 LEARNING OUTCOMES

Introduction

a) Give the name of hydroxy compounds according to the IUPAC nomenclature. (C2)

b) Give the structural formulae for the hydroxy compounds (parent chain ≤ C_{10}). (C2)

c) classify the hydroxy compounds (C2)

INTRODUCTION TO ALCOHOLS

- **Contain hydroxyl group (-OH) bonded to sp^3 hybridized C atom.**

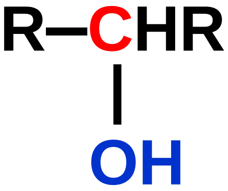
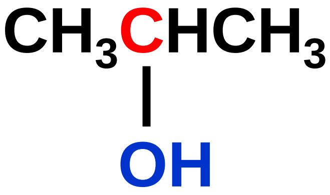
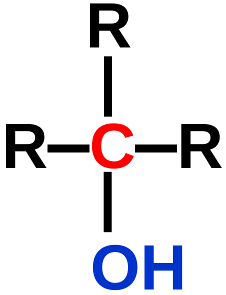
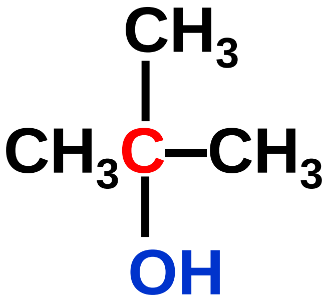
- **Aliphatic alcohol**

General formula : R—OH

☞ $C_nH_{2n+1}OH$

CLASSIFICATION OF ALCOHOLS

- ❑ Depending on type of C atom to which the –OH group is directly attached.

CLASS	GENERAL FORMULA	EXAMPLE
1^o	$R-OH$	CH_3CH_2OH
2^o	 $R-\underset{\underset{OH}{\vert}}{C}HR$	 $CH_3\underset{\underset{OH}{\vert}}{C}HCH_3$
3^o	 $R-\overset{\overset{R}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-R$	 $CH_3\overset{\overset{CH_3}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-CH_3$

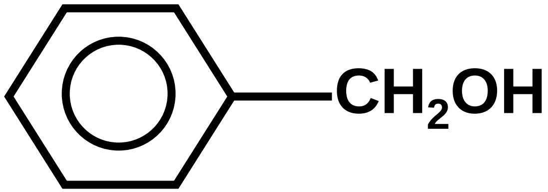
EXERCISE 1

Classify the types of alcohol (1^{o}, 2^{o} or 3^{o}) for the following molecules.

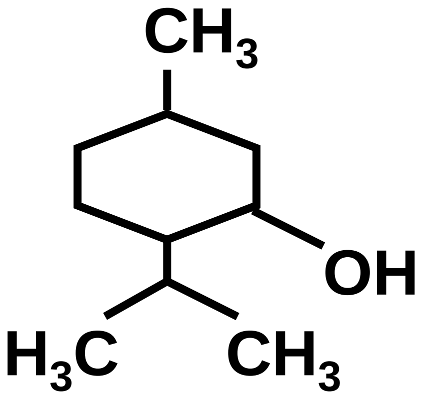
(a) $CH_3CH(OH)CH_3$

(b) $(CH_3)_2C(OH)CH_2CH_3$

(c)



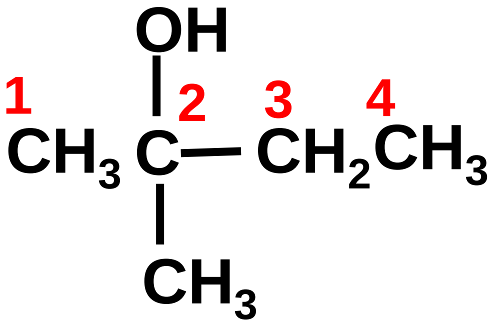
(d)



NOMENCLATURE OF ALCOHOLS

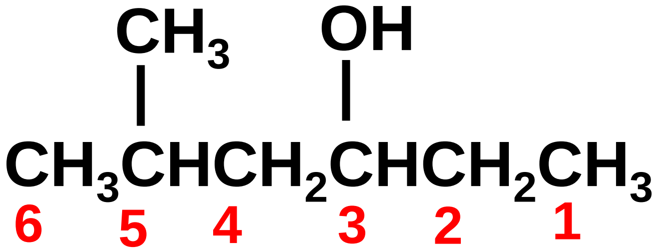
1) Find the ***longest C chain*** containing the **OH.**
2) Give the –**OH** group the **lowest number**.
3) Identify substituent groups and their position.
4) The substituent are arranged in **alphabetical order**.
5) The **suffix** '–e' in the alkane parent name is replaced by **'–ol'**.

Example:



$CH_3C(OH)(CH_3)CH_2CH_3$

2–methyl–2–butanol

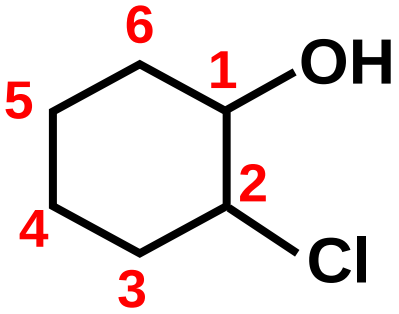


$CH_3CH(CH_3)CH_2CH(OH)CH_2CH_3$

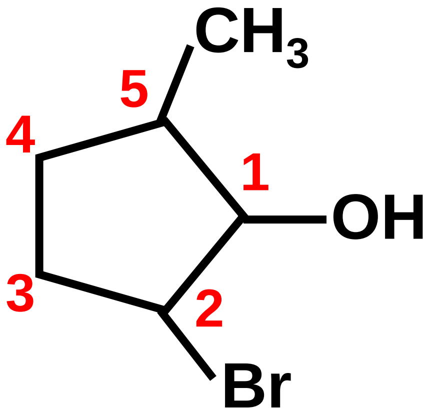
5–methyl–3–hexanol

6) Ring/Cyclic: Numbering start at **C bearing OH.**

EXAMPLE:

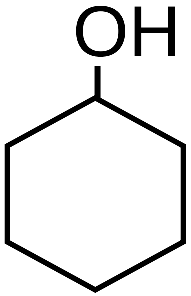


2–chlorocyclohexanol



2–bromo–5–methylcyclopentanol

Example:

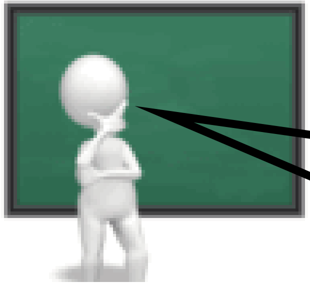
Structure	Common name	**IUPAC name**
CH_3OH	methyl alcohol	**methanol**
CH_3CH_2OH	ethyl alcohol	**ethanol**
$CH_3CH(OH)CH_3$	isopropyl alcohol	**2-propanol**
	cyclohexyl alcohol	**cyclohexanol**

Keep in mind!

EXAMPLE:

$CH_3CH_2CH_2CH_2OH$

- **1979 IUPAC recommendation:** **1–butanol**
- **1993 IUPAC recommendation:** **butan–1–ol**



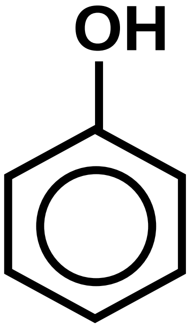
The first of these convention
☞ 1–butanol is more widely used

7) Aromatic alcohol – phenol

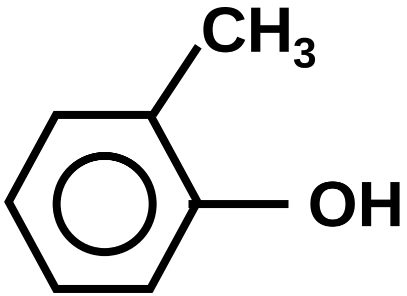
(-OH group attached directly to benzene ring)

For **phenol**, C attach to the –OH group is C1.

Example:



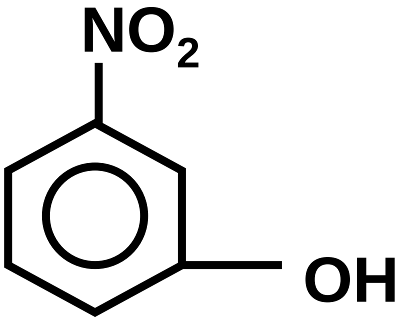
phenol



2-methylphenol

or

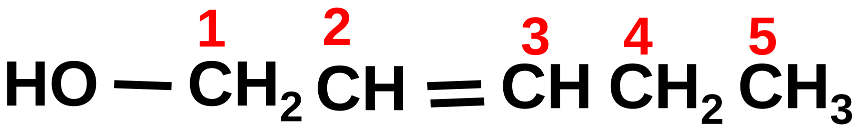
o-methylphenol



3–nitrophenol or m–nitrophenol

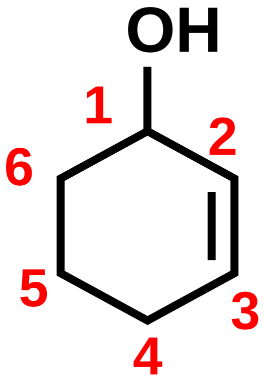
8) –OH has priority over C=C

EXAMPLE:



$$\mathrm{HO}-\overset{1}{\mathrm{CH_2}}\overset{2}{\mathrm{CH}}=\overset{3}{\mathrm{CH}}\,\overset{4}{\mathrm{CH_2}}\,\overset{5}{\mathrm{CH_3}}$$

2–penten–1–ol or **pent–2–en–1–ol**



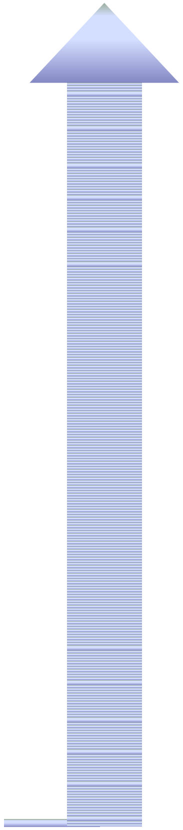
2–cyclohexen–1–ol

or

cyclohex–2–en–1–ol

Keep in mind!

Increasing PRIORITY
fo parent name



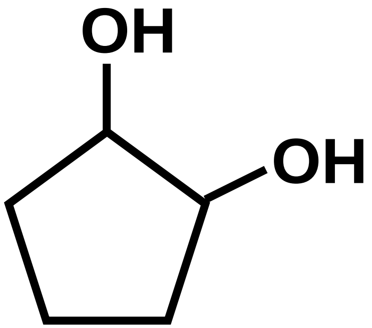
MAIN GROUPS
carboxylic acids
esters
aldehydes
ketones
alcohol
amine
alkenes
alkanes / halides

9) Two OH groups ☞ diol

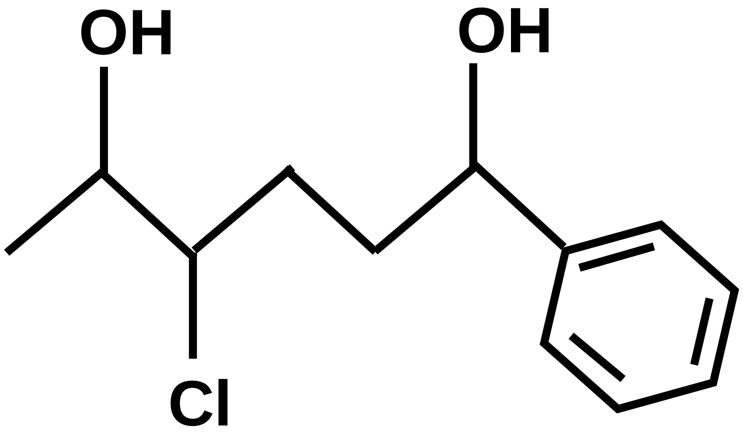
EXAMPLE:

$HOCH_2CH_2OH$

1,2–ethanediol



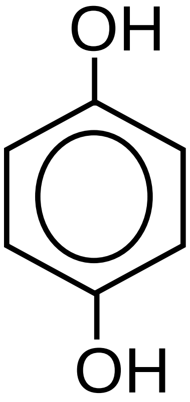
1,2–cyclopentanediol



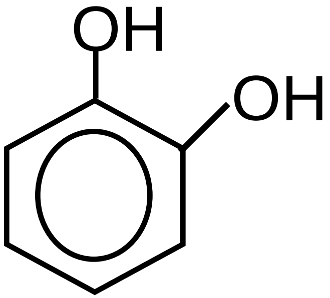
4–chloro–1–phenyl–1,5–hexanediol

10) If two or more –OH on the **aromatic ring**:

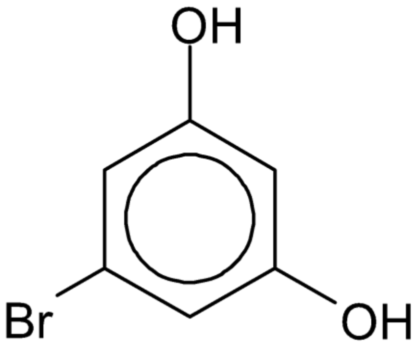
Benzene derivatives with two –OH groups are name as **benzenediol**



Benzene-1,4-diol



Benzene-1,2-diol

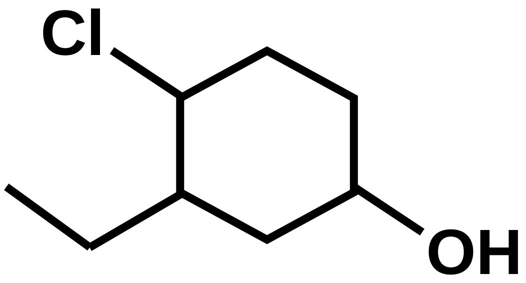


5-bromobenzene-1,3-diol

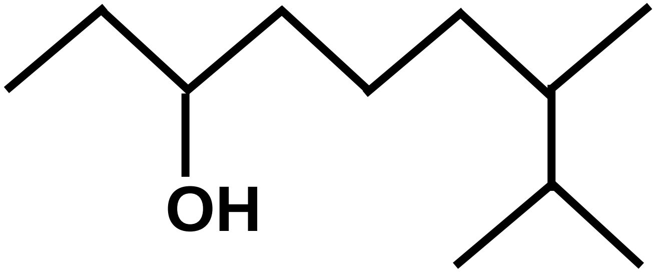
EXERCISE 2

Give the IUPAC names of the following compounds.

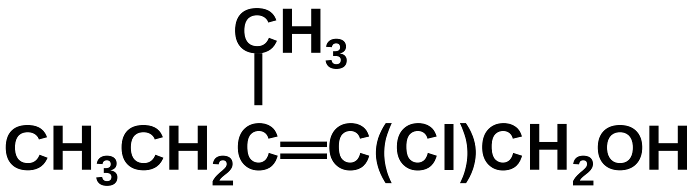
(a)



(b)

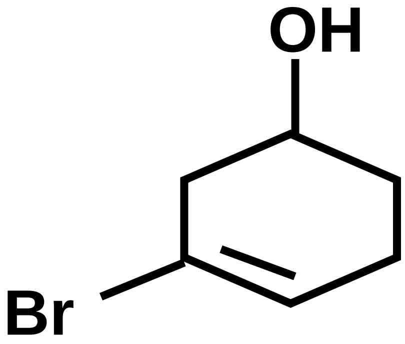


(c)



$CH_3CH_2\overset{\overset{CH_3}{|}}{C}=C(Cl)CH_2OH$

(d)



(e) $HO—(CH_2)_8—OH$

8.2 LEARNING OUTCOMES

Physical properties:

a) Explain the physical properties:(C3,C4)

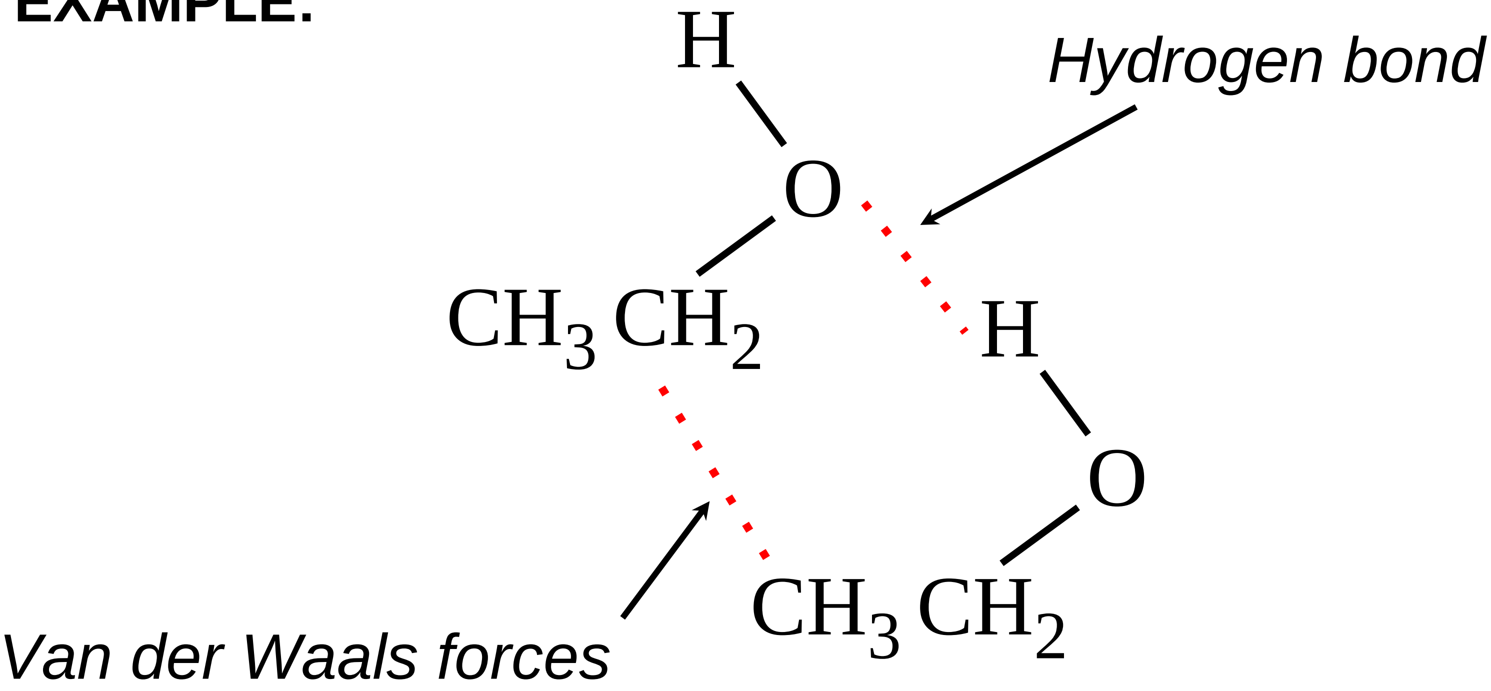
(i) boiling point

(ii) solubility in water

BOILING POINT

- In liquid form, molecules of alcohol can form **hydrogen bond** between OH group and also **van der Waals forces** between alkyls group.

EXAMPLE:



- As **molecular weight increase** (**size of molecule increase**), the **strength of van der Waals forces increase**, thus the **boiling point** will **increase**.

EXAMPLE:

Compound	Molecular weight (gmol^{-1})	Boiling Point (^oC)
Ethanol (2C) CH_3CH_2OH	*46*	*78*
1-butanol (4C) $CH_3CH_2CH_2CH_2OH$	*74*	*118*

- When the **number of −OH groups increases**, **boiling point increases**.

  - This is due to the *formation of more hydrogen bonds* between alcohol molecules

Example:

Compound	Boiling Point (^{o}C)
1,2-ethanediol $\mathbf{HO}CH_2CH_2\mathbf{OH}$	198
1-propanol $CH_3CH_2CH_2\mathbf{OH}$	97

- ❑ Alcohols have higher boiling points than alkanes of similar molecular weight.
  - ➢ alcohols form hydrogen bond between molecules while alkanes only form weak van der Waals forces between molecules.
- ❑ Hydrogen bond is stronger than van der Waals forces.

Example:

Compound	Molecular weight ($gmol^{-1}$)	Boiling Point (^{o}C)
Ethanol CH_3CH_2OH	46	78
Propane $CH_3CH_2CH_3$	44	-42

- For compounds of **comparable molecular** size, the **stronger the intermolecular forces**, the **higher the boiling point**.

EXAMPLE:

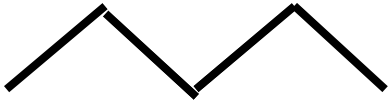
$CH_3CH_2CH_2CH_3$,	$CH_3OCH_2CH_3$,	$CH_3CH_2CH_2OH$
London Force	**Dipole dipole London Force**	**Hydrogen bond Dipole dipole London Force**

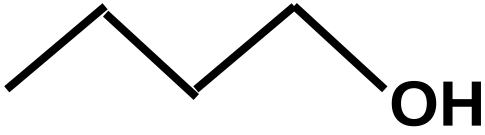
Increasing BOILING POINT →

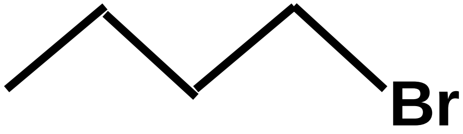
EXERCISE 3:

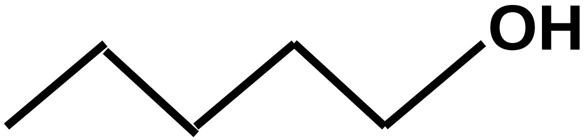
Rank the compounds in each group in order of increasing boiling point.

(a)







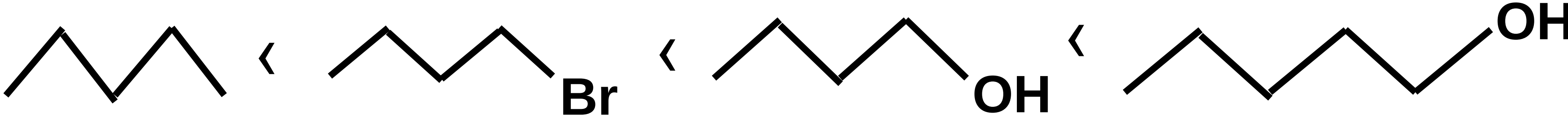


(b) $(CH_3)_3COC(CH_3)_3$ $CH_3(CH_2)_3O(CH_2)_3CH_3$

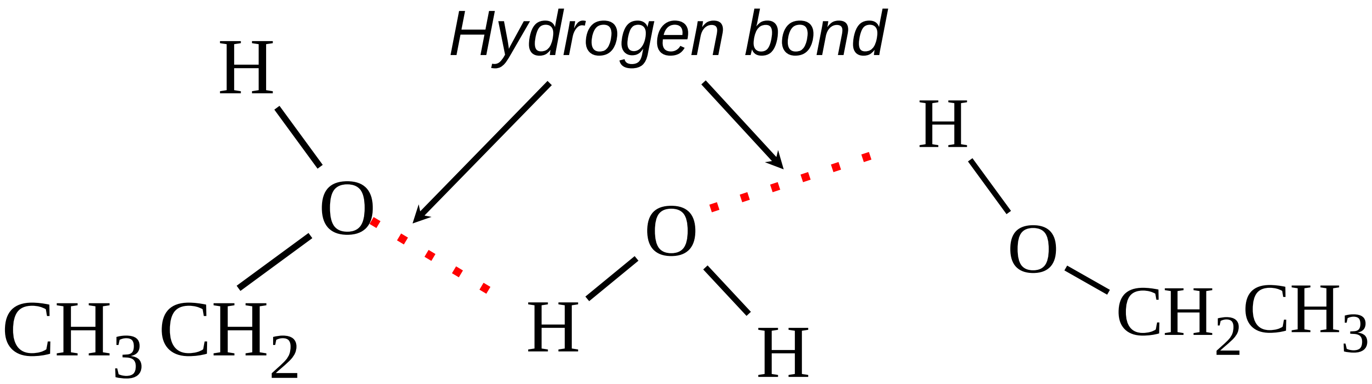
$CH_3(CH_2)_7OH$

ANSWER

(a)



SOLUBILITY



- ≤ 5 C: water soluble
  - Capable of H bonding to H_2O
- > 5 C: water insoluble
  - Non polar (hydrophobic) alkyl portion is too large to dissolve in H_2O

- **The alkyl group are hydrophobic and the hydroxyl group are hydrophilic.**
- **As the size of alkyl group increases, the hydrophobic area increases, thus solubility decrease.**

$$\underbrace{\mathbf{R\text{-}CH_2}}_{\text{Hydrophobic area}}\overbrace{\mathbf{\text{-}OH}}^{\text{Hydrophilic area}}$$

hydrophobic

hydrophilic

ALKYL (R) — OH

WATER SOLUBILITY OF ALCOHOLS (AT 25°C)	
ALKYL	SOLUBILITY
methyl	miscible
ethyl	miscible
propyl	miscible
tert-butyl	miscible
isobutyl	10.0%
butyl	9.1%
pentyl	2.7%
hexane–1,6–diol	miscible

❑ **For alcohols with comparable molecular weight,**

- **solubility increase with increasing number of –OH groups.**

- **able to form more hydrogen bonds with H_2O molecules.**

EXAMPLE:

Solubility : $HO(CH_2)_6OH$ > $CH_3(CH_2)_5OH$

☞ **two OH groups** ☞ **one OH group**

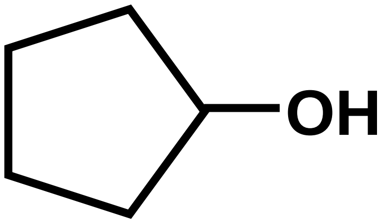
☞ **can form more H bonding with water**

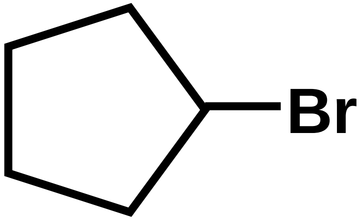
EXAMPLE:

Compare the solubility in water for the following compounds.

(a) $CH_3CH_2CH_2CH_3$ $CH_3CH_2CH_2OH$

(b)





(c) $CH_3CH_2CH_2CH_2OH$ $HOCH_2CH_2OH$

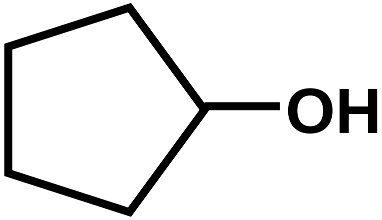
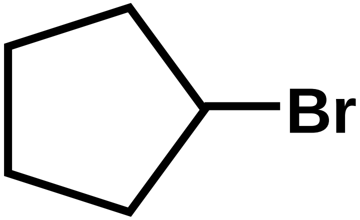
ANSWER:

(a) **Ability to form hydrogen bonding with H_2O:**

$CH_3CH_2CH_2CH_3$ an alkane	**Can’t form hydrogen bond with water** ☛ **Insoluble in water**
$CH_3CH_2CH_2OH$ an alcohol	**Can form hydrogen bond with water** ☛ **Soluble in water**

ANSWER:

(b)

		
	an alcohol	an alkyl halide
Ability to form H bonding with H_2O:	**YES**	**NO**
Solubility in water	**Soluble**	**insoluble**

ANSWER :

(c) $CH_3CH_2CH_2CH_2OH$ $HOCH_2CH_2OH$

Solubility : $HOCH_2CH_2OH > CH_3CH_2CH_2CH_2OH$

☞ two OH groups

☞ one OH group

☞ can form more H bonding with water

PHYSICAL PROPERTIES OF PHENOLS

- Strongly influenced by hydroxy group (-OH)
- has higher melting point and boiling point than alkanes, arenes and aryl halides of comparable molecular size.
- slightly soluble in water but has higher solubility than alkanes, arenes and aryl halides of comparable molecular size.

8.3 LEARNING OUTCOMES

Preparation of alcohols (C3,C4)

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

8.3 PREPARATION OF ALCOHOLS

Explain the preparation of alcohol by

- Fermentation
  - A biological process of enzymatic degradation of sugars by microorganisms

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2CH_3CH_2OH \quad + \quad 2CO_2$$

- Hydration of Alkenes
- Hydrolysis of Haloalkanes
  - Reaction with NaOH
  - Reaction with H_2O
- Addition of Grignard reagents to carbonyl compounds.
  - Preparation of 1° alcohol
  - Preparation of 2° alcohol
  - Preparation of 3° alcohol

PREPARATION OF ALCOHOLS

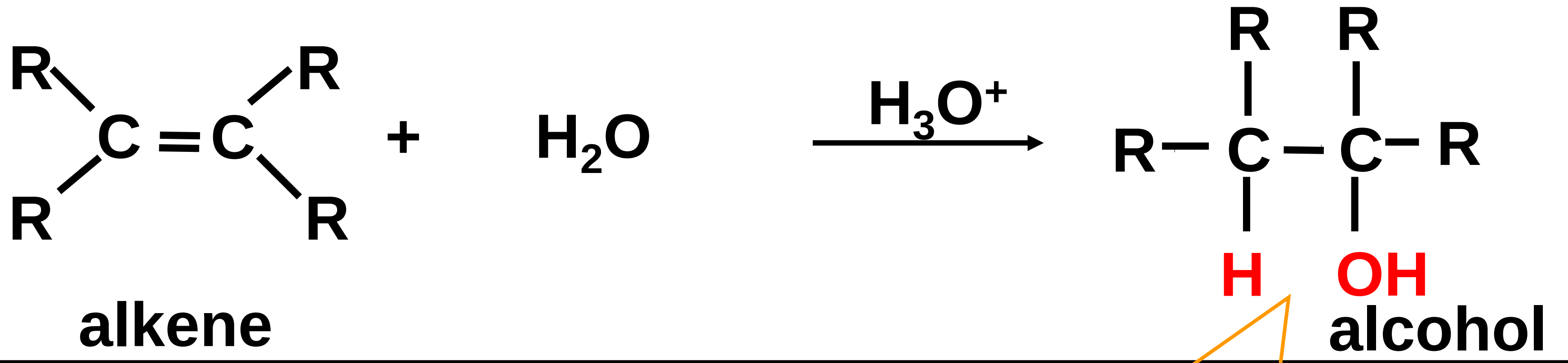
1) Fermentation

- A biological process of enzymatic degradation of sugars by microorganisms

$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{yeast}} \underset{\text{ethanol}}{2CH_3CH_2OH} + 2CO_2$$

2) Hydration of Alkenes

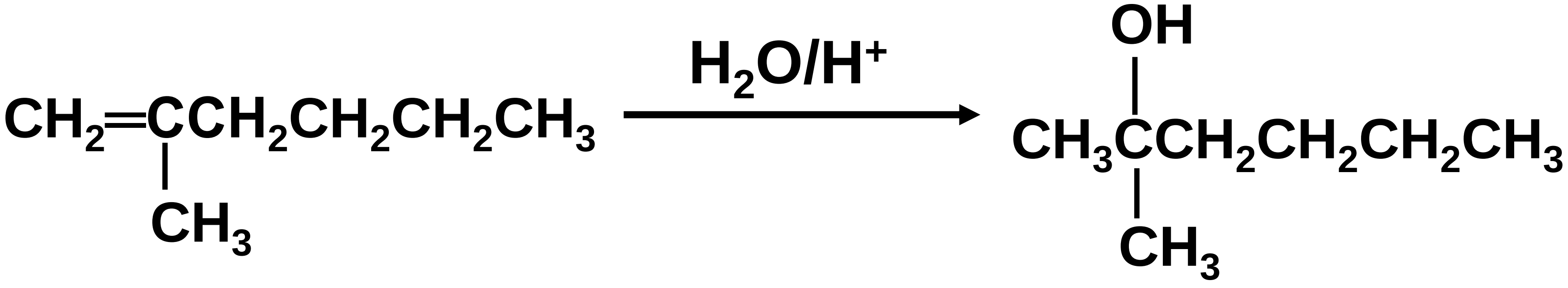
- Method for preparation of simple alcohol.
- Reactant : Alkene and water
- Condition : Catalyst (H_2SO_4)



H and OH added!

- Follow Markovnikov’s Rule

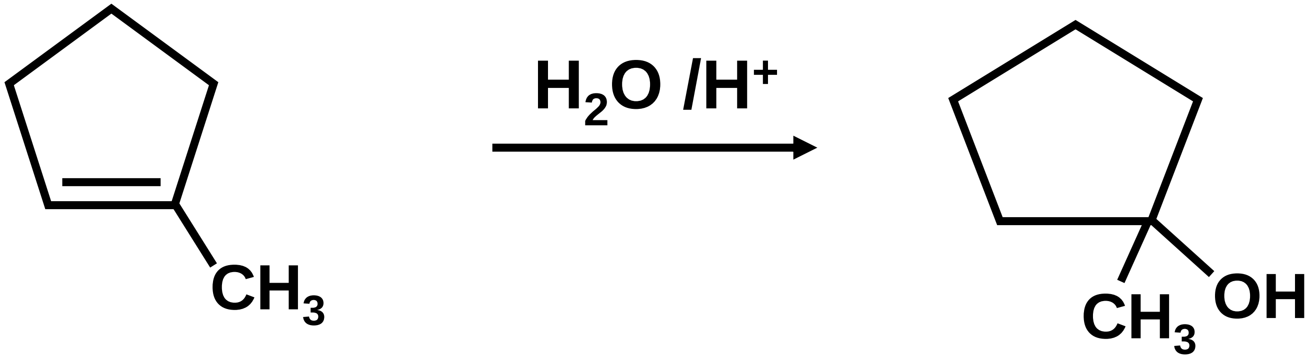
EXAMPLE:



$$CH_2{=}C(CH_3)CH_2CH_2CH_2CH_3 \xrightarrow{H_2O/H^+} CH_3C(OH)(CH_3)CH_2CH_2CH_2CH_3$$

2–methyl–1–hexene

2–methyl–2–hexanol



1–methylcyclopentene

1–methylcyclopentanol

3) Hydrolysis of haloalkanes

- **Reactant: haloalkane and NaOH or H_2O**

$$R—X \quad + \quad {}^{-}OH \longrightarrow R—OH \quad + \quad X^{-}$$

alcohol

Substitute X with OH

EXAMPLE:

$$CH_3CH_2—Br \quad + \quad NaOH_{(aq)} \longrightarrow CH_3CH_2—OH \quad + \quad NaBr$$

1^0 haloalkane

bromoethane

Strong Nucleophile

ethanol

$$(CH_3)_3C–Cl \quad + \quad H_2O \longrightarrow (CH_3)_3C–OH \quad + \quad HCl$$

3^0 haloalkane

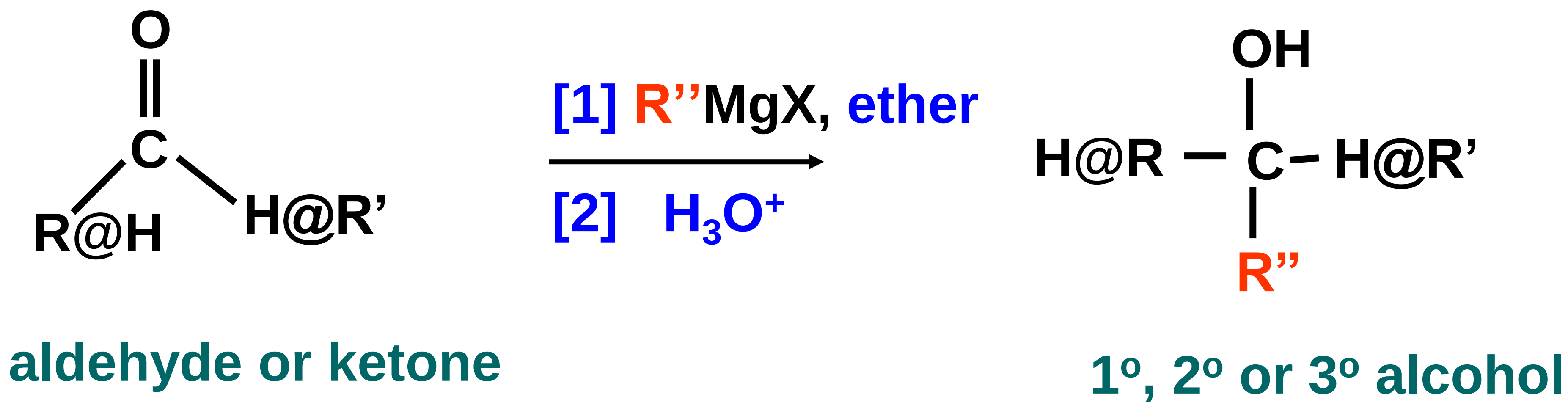
weak Nu

2–chloro–2–methylpropane

2–methyl–2–propanol

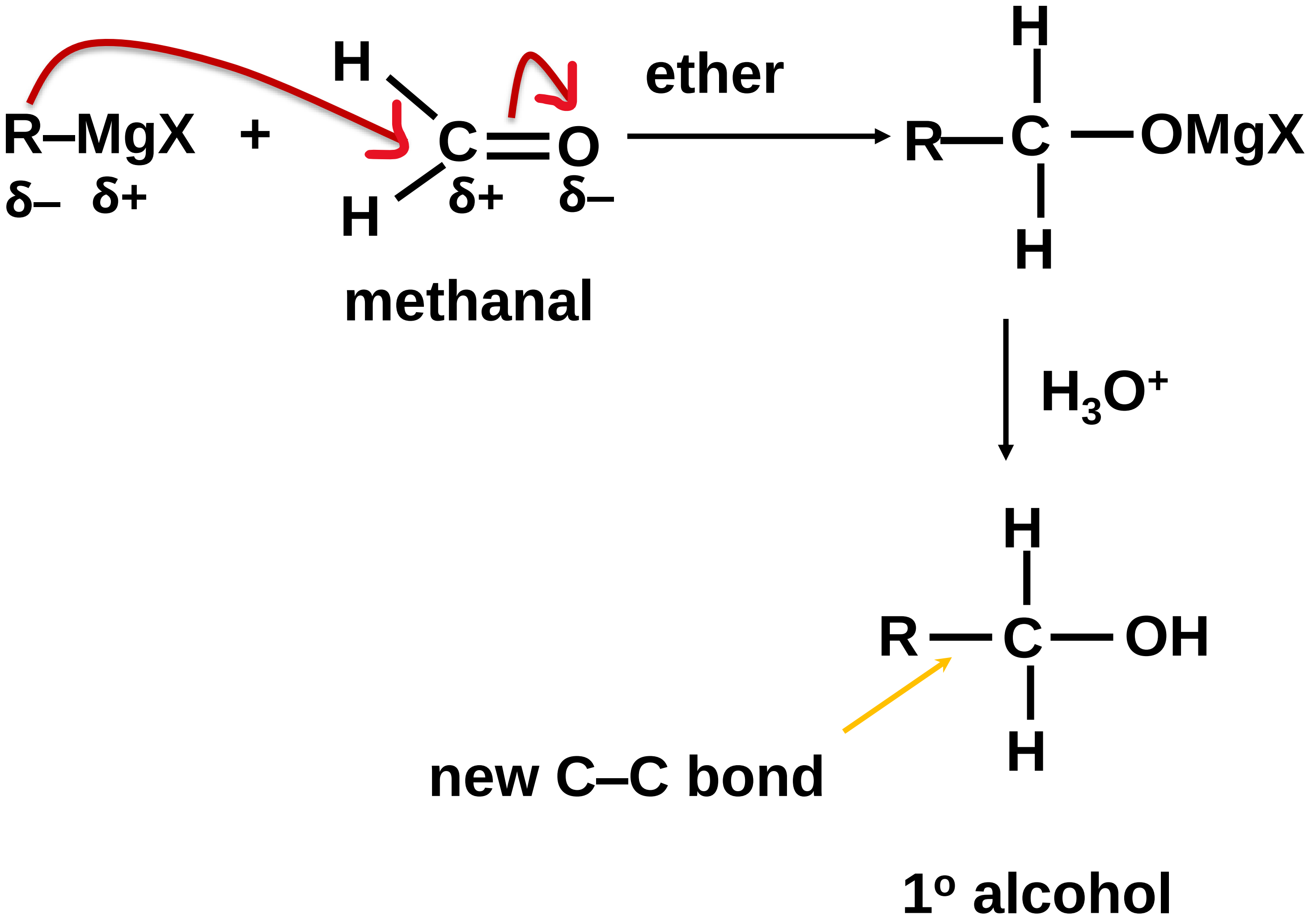
4) Addition of Grignard reagent to carbonyl compounds

- 1^o, 2^o & 3^o alcohols can be prepared by addition of Grignard reagent with carbonyl compounds followed by hydrolysis.

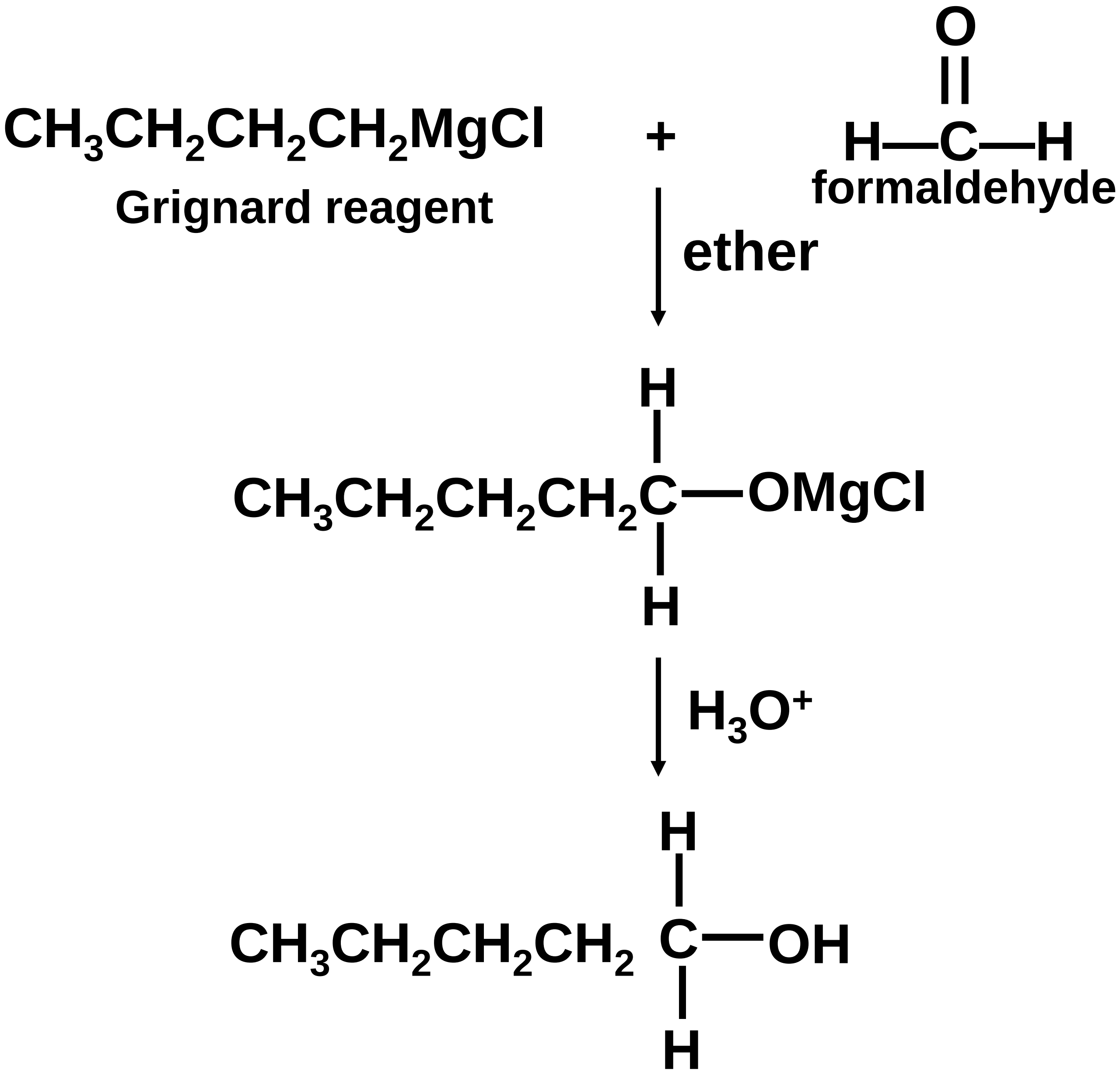


(a) Formation of 1º alcohols

(Grignard reagent + methanal @ formaldehyde)



EXAMPLE:

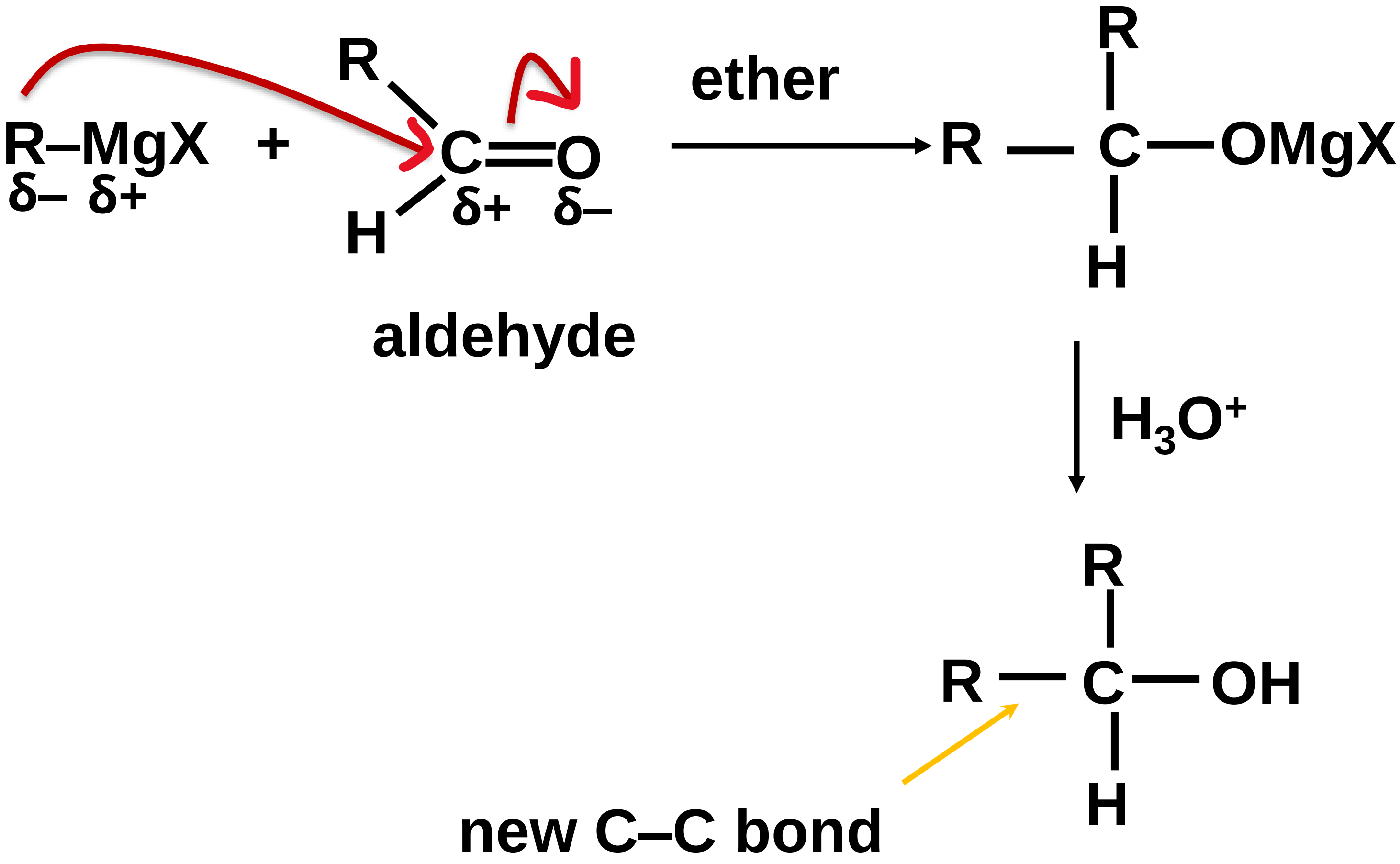


$$CH_3CH_2CH_2CH_2MgCl + H{-}\overset{\overset{\Large O}{\|}}{C}{-}H \xrightarrow{\text{ether}} CH_3CH_2CH_2CH_2\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}OMgCl \xrightarrow{H_3O^+} CH_3CH_2CH_2CH_2\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}OH$$

1–pentanol

(b) Formation of 2° alcohols

(Grignard reagent + aldehyde)

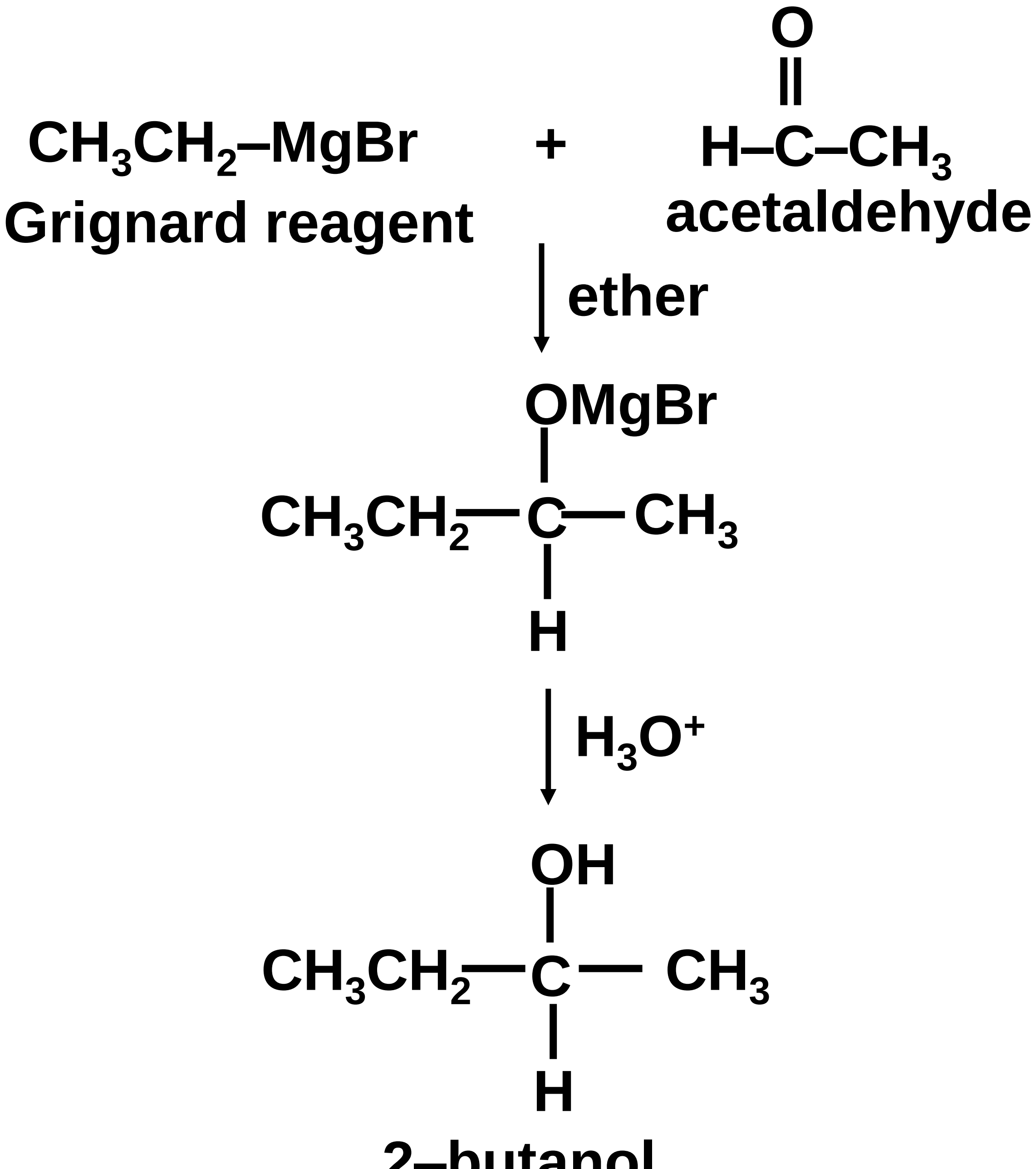


aldehyde

new C–C bond

2° alcohol

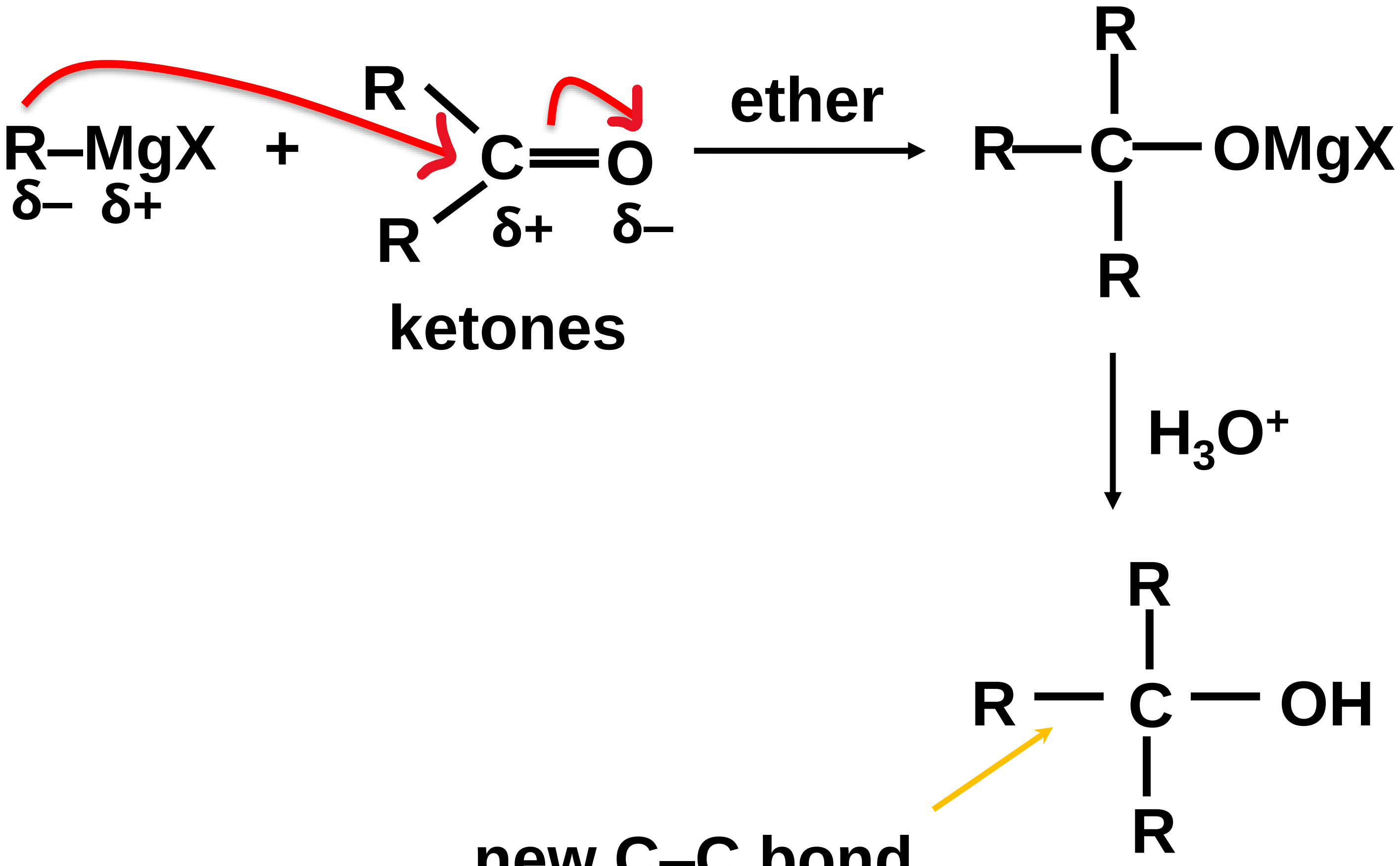
EXAMPLE:



$$\underset{\text{Grignard reagent}}{\mathrm{CH_3CH_2{-}MgBr}} + \underset{\text{acetaldehyde}}{\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}CH_3}} \xrightarrow{\text{ether}} \mathrm{CH_3CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{OMgBr}{|}}{C}}{-}CH_3} \xrightarrow{H_3O^+} \underset{\text{2–butanol}}{\mathrm{CH_3CH_2{-}\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}{-}CH_3}}$$

(c) Formation of 3° alcohol

(Grignard reagent + ketone)

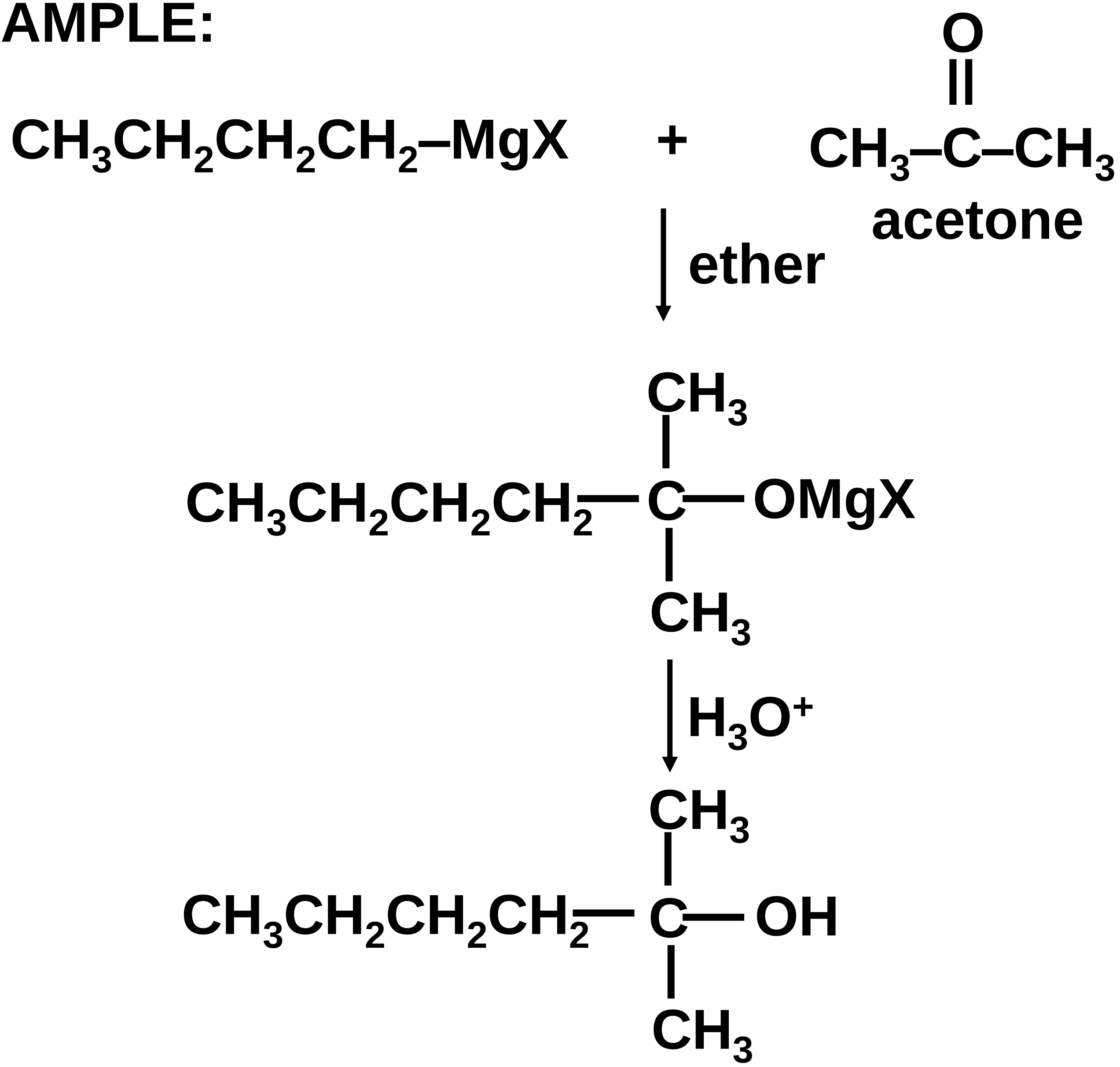


ketones

new C–C bond

3° alcohol

EXAMPLE:

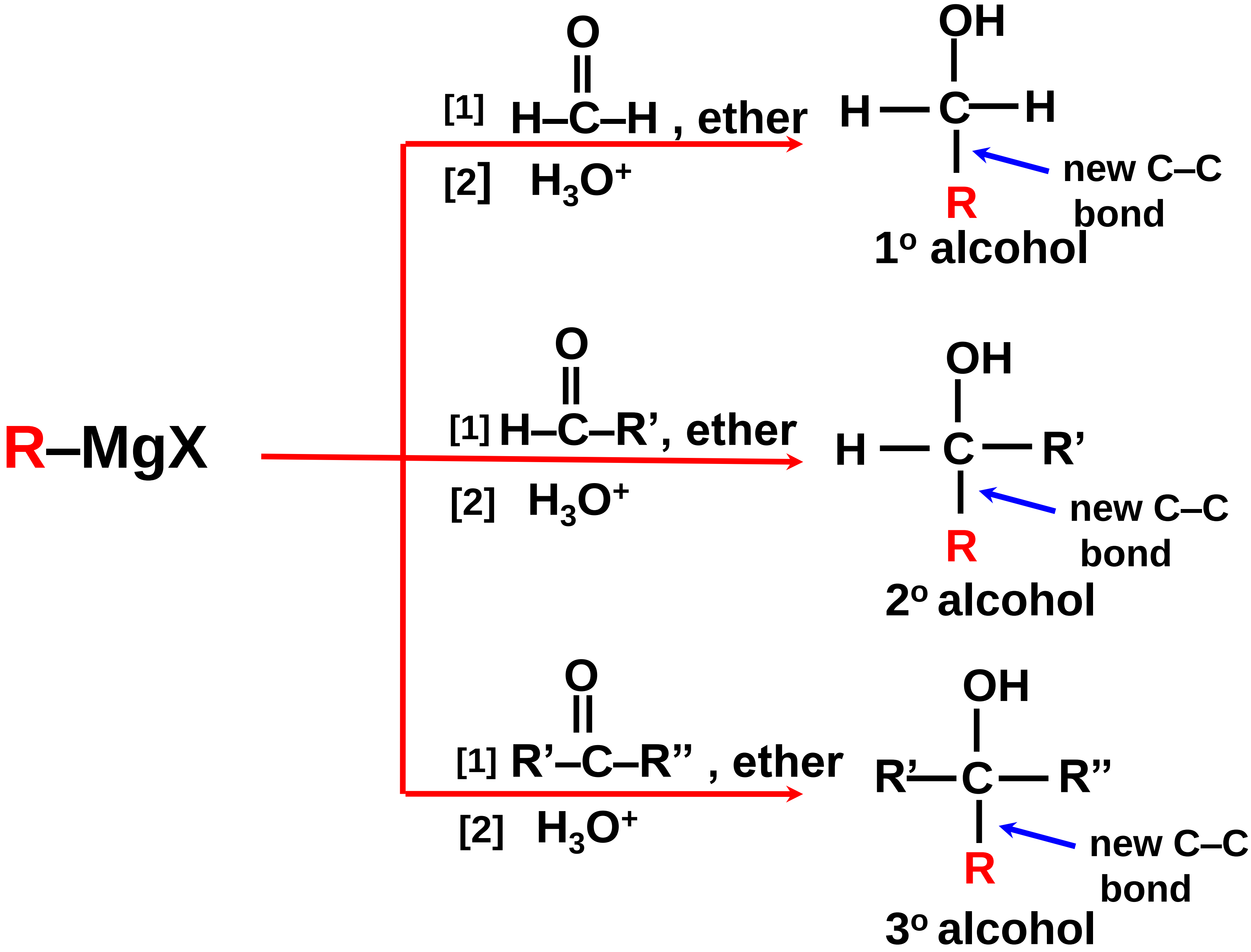


$$CH_3CH_2CH_2CH_2{-}MgX \; + \; CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$$

acetone

$$\xrightarrow{\text{ether}} \quad CH_3CH_2CH_2CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}OMgX \quad \xrightarrow{H_3O^+} \quad CH_3CH_2CH_2CH_2{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}OH$$

2–methyl–2–hexanol



R–MgX

[1] $H-\overset{\overset{\large O}{\|}}{C}-H$, ether

[2] H_3O^+

$$H-\overset{\overset{\large OH}{|}}{\underset{\underset{\large R}{|}}{C}}-H$$

new C–C bond

1° alcohol

[1] $H-\overset{\overset{\large O}{\|}}{C}-R'$, ether

[2] H_3O^+

$$H-\overset{\overset{\large OH}{|}}{\underset{\underset{\large R}{|}}{C}}-R'$$

new C–C bond

2° alcohol

[1] $R'-\overset{\overset{\large O}{\|}}{C}-R''$, ether

[2] H_3O^+

$$R'-\overset{\overset{\large OH}{|}}{\underset{\underset{\large R}{|}}{C}}-R''$$

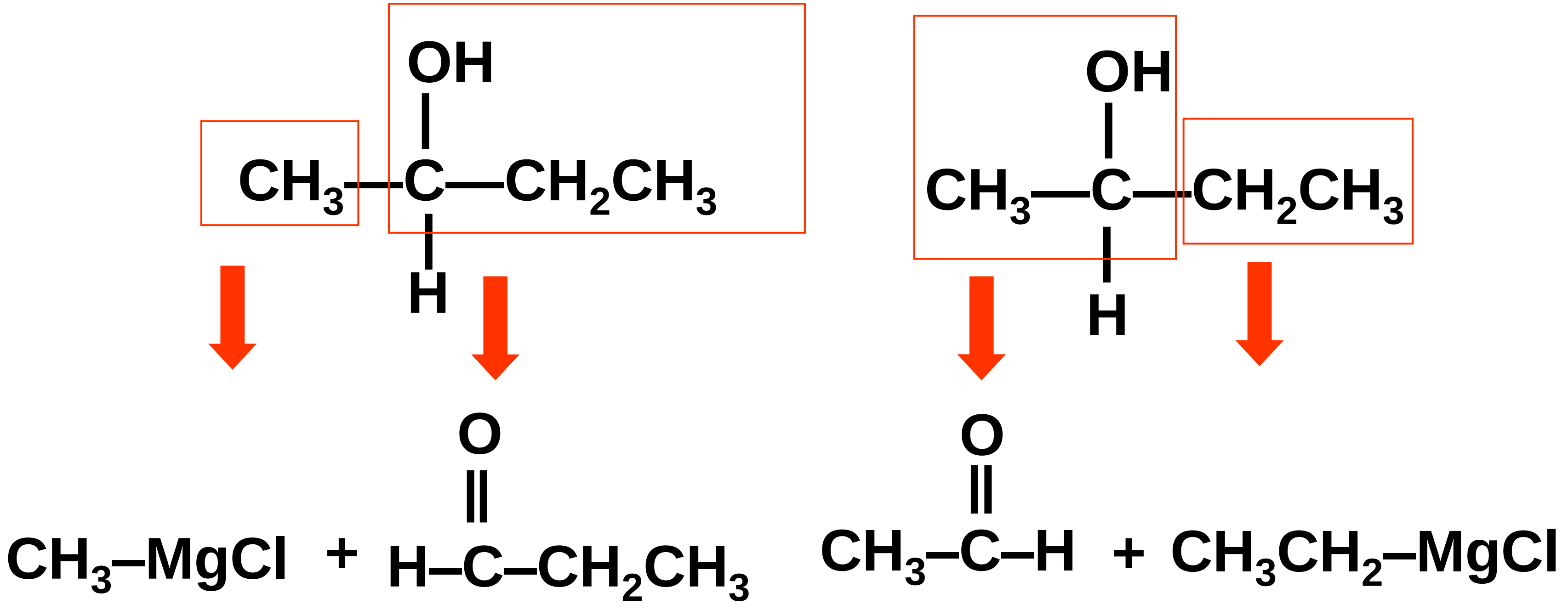
new C–C bond

3° alcohol

Keep in mind!

❑ **Sometimes, there are two or three possibilities to prepare alcohol using Grignard reagent**

EXAMPLE: preparation of 2–butanol



$$CH_3-\underset{H}{\overset{OH}{C}}-CH_2CH_3 \qquad CH_3-\underset{H}{\overset{OH}{C}}-CH_2CH_3$$

$$CH_3-MgCl + H-\overset{O}{\overset{\|}{C}}-CH_2CH_3 \qquad CH_3-\overset{O}{\overset{\|}{C}}-H + CH_3CH_2-MgCl$$

8.4 LEARNING OUTCOMES

Chemical properties of alcohols

a) Explain the reactions of alcohol with reference to:(C3,C4)

- (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 (C3,C4)

c) Explain the identification tests to distinguish classes of alcohols using Lucas reagent, i.e. concentrated $HCl/ZnCl_2$ (C3,C4)

d) Explain iodoform test, i.e. I_2/OH^- to identify methyl carbinol $CH_3CH(OH)$-. (C3,C4)

d) Outline the synthesis of compounds involving alcohols (C4)

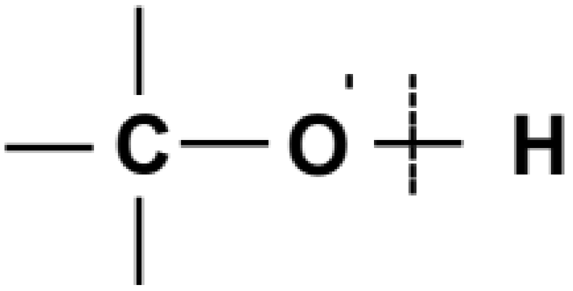
** Limit to maximum 4 steps only*

8.4 CHEMICAL PROPERTIES OF ALCOHOLS

- Chemical Properties of Alcohols
  - Reactions of Alcohol
    - **Reaction with sodium, Na**
    - **Substitution Reaction HX, PX_3, PCl_5, $SOCl_2$**
    - **Esterification**
    - **Dehydration**
  - Oxidation of Alcohols
    - **Acidified solution of chromate**
    - **Acidified solution of permanganate**
    - **Pyridinium chlorochromate, PCC**
  - Identification Test
    - **Lucas Test**
  - Iodoform Test
    - **To identify methyl carbinol**

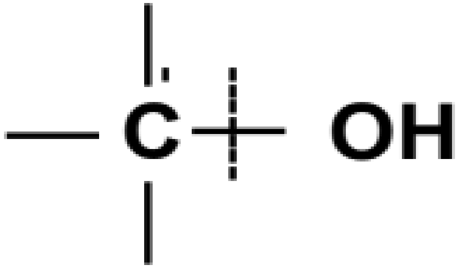
TYPES OF REACTIONS OF HYDROXY COMPOUNDS

1) **Cleavage of bond between O and H in -OH group (O-H bond is broken in R-O-H):**



- **(a) Reaction with Na**
- **(b) Esterification**
- **(c) Oxidation**

2) Cleavage of bond between C and O (C-OH bond is broken in R-O-R):



(a) Dehydration

(b) Substitution reaction using :
HX, PX_3, PCl_5 or $SOCl_2$

(A) REACTION WITH SODIUM

- **Reactant** : alcohol and Na
- **Product** : sodium alkoxide and H_2 gas

$$R\text{—}O\text{—}H \quad + \quad Na \longrightarrow R\text{—}O^{-}\,Na^{+} \quad + \quad \tfrac{1}{2}\,H_2\uparrow$$

sodium alkoxide

The alcohol acts as an acid

EXAMPLE:

$$CH_3CH_2OH \quad + \quad Na \longrightarrow CH_3CH_2O^{-}Na^{+} \quad + \quad \tfrac{1}{2}H_2\uparrow$$

ethanol

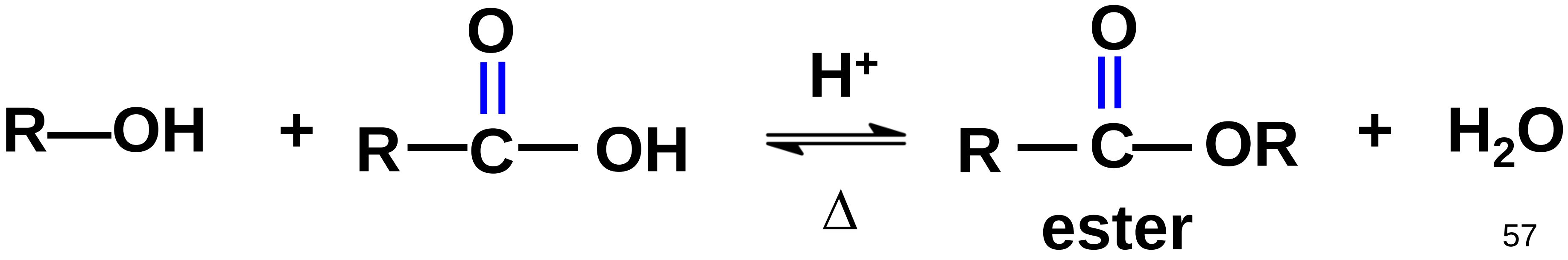
sodium ethoxide

(B) ESTERIFICATION

❑ Reactant : carboxylic acid and alcohol

❑ Condition :
- Reflux
- Catalyst (H_2SO_4 or HCl)

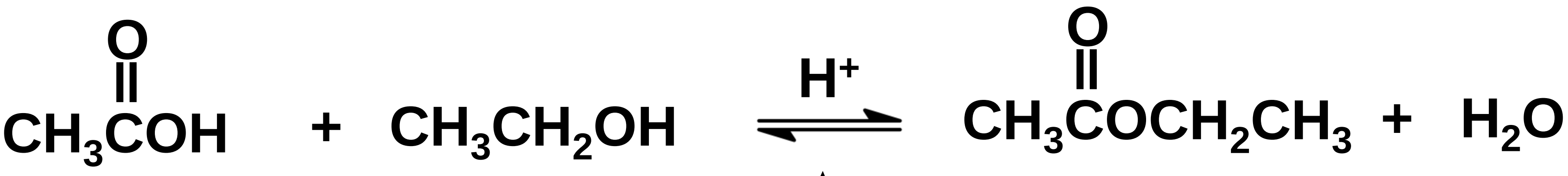
❑ Product : ester and H_2O



$$R\text{—}OH + R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH \xrightleftharpoons[\Delta]{H^+} R\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OR + H_2O$$

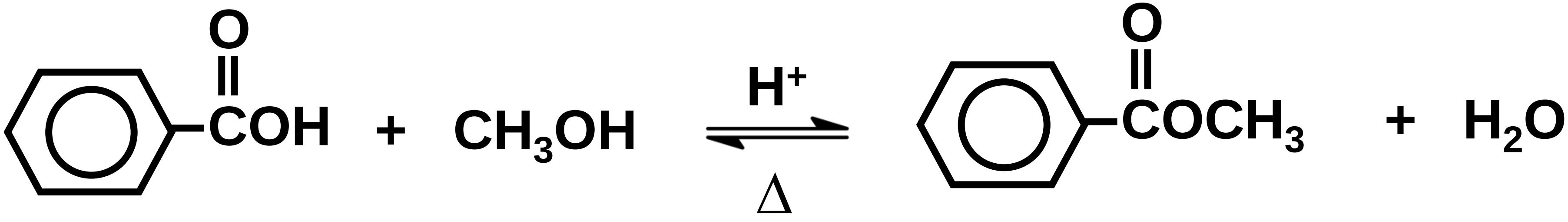
ester

EXAMPLE:



$$CH_3\overset{O}{\overset{\|}{C}}OH + CH_3CH_2OH \underset{\Delta}{\overset{H^+}{\rightleftharpoons}} CH_3\overset{O}{\overset{\|}{C}}OCH_2CH_3 + H_2O$$

acetic acid ethanol ethyl acetate



benzoic acid methanol methyl benzoate

(C) OXIDATION

☐ **Oxidizing agent:**

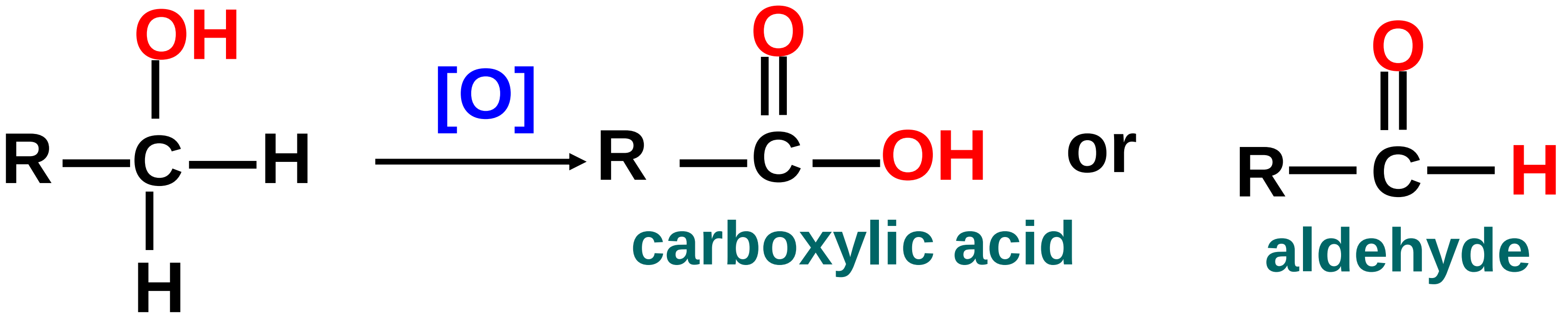
- **Acidified solution of chromate ($Na_2Cr_2O_7$, $K_2Cr_2O_7$, CrO_3)**
- **Acidified solution of permanganate ($KMnO_4$)**
- **Pyridinium chlorochromate (PCC) in CH_2Cl_2**

☐ **Oxidation product depends on the class of alcohol used and types of oxidizing agent.**

Oxidation of 1º alcohol

- ❑ 1º alcohols are oxidized to aldehydes or carboxylic acids, depending on the reagent:

Oxidising Agent	Product
PCC in CH_2Cl_2 (mild condition)	aldehyde
Hot acidified $KMnO_4$, $Na_2Cr_2O_7$, $K_2Cr_2O_7$, or CrO_3 (harsher condition)	carboxylic acid



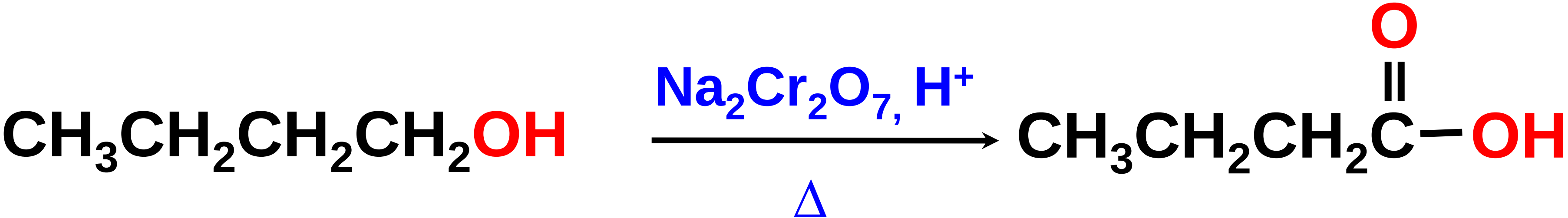
$$R-CH_2-OH \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-OH \text{ or } R-\overset{O}{\overset{\|}{C}}-H$$

1° alcohol

carboxylic acid

aldehyde

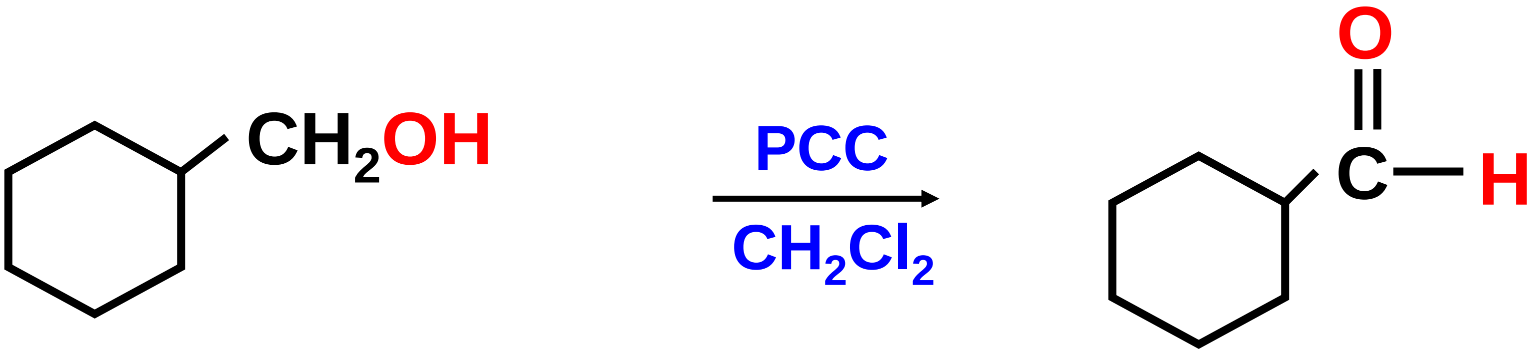
EXAMPLE:



$$CH_3CH_2CH_2CH_2OH \xrightarrow[\Delta]{Na_2Cr_2O_{7,}\ H^+} CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}-OH$$

1–butanol

butanoic acid



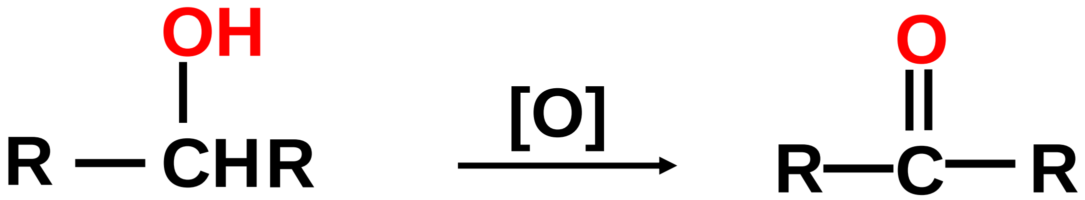
$\xrightarrow[CH_2Cl_2]{PCC}$

cyclohexyl methanol

cyclohexanal

Oxidation of 2º alcohol

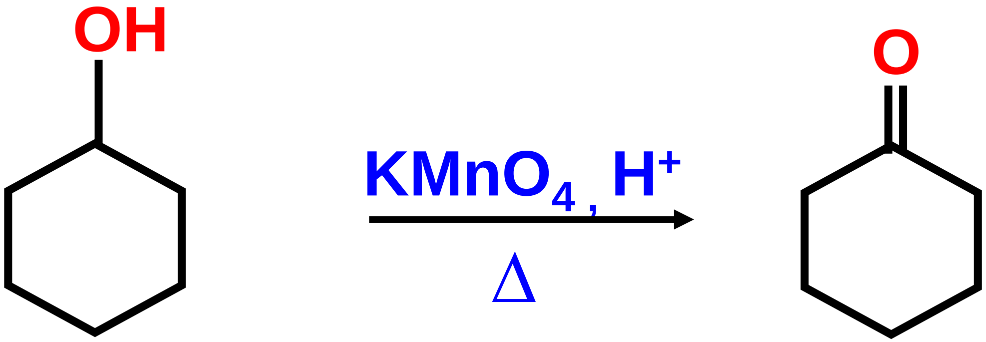
- ❑ 2º alcohol is oxidised to ketone



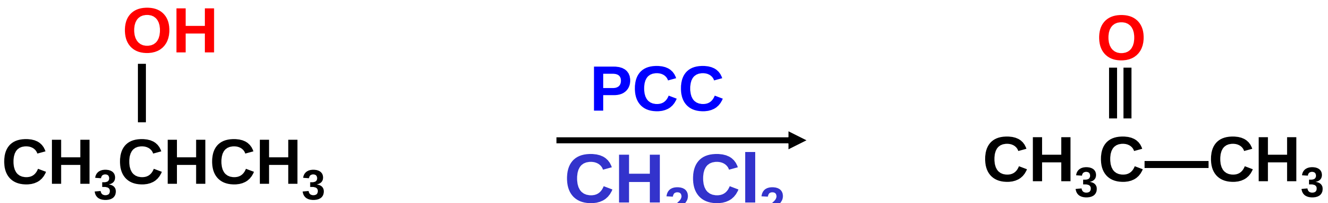
$$R-\overset{OH}{\overset{|}{C}}HR \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-R$$

2º alcohol ketone

EXAMPLE:



cyclohexanol cyclohexanone

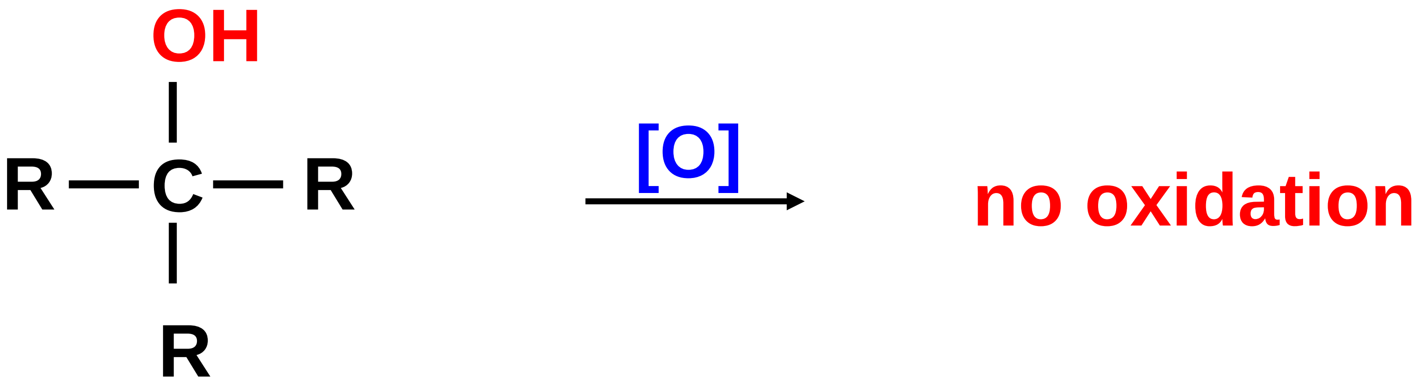


$$CH_3\overset{OH}{\overset{|}{C}}HCH_3 \xrightarrow[CH_2Cl_2]{PCC} CH_3\overset{O}{\overset{\|}{C}}-CH_3$$

2–propanol propanone

Oxidation of 3° alcohol

- 3° alcohol does not undergo oxidation under normal condition.
  - have no C–H bond on the C bearing the OH group.



$$R-\overset{\overset{OH}{|}}{\underset{\underset{R}{|}}{C}}-R \xrightarrow{[O]} \text{no oxidation}$$

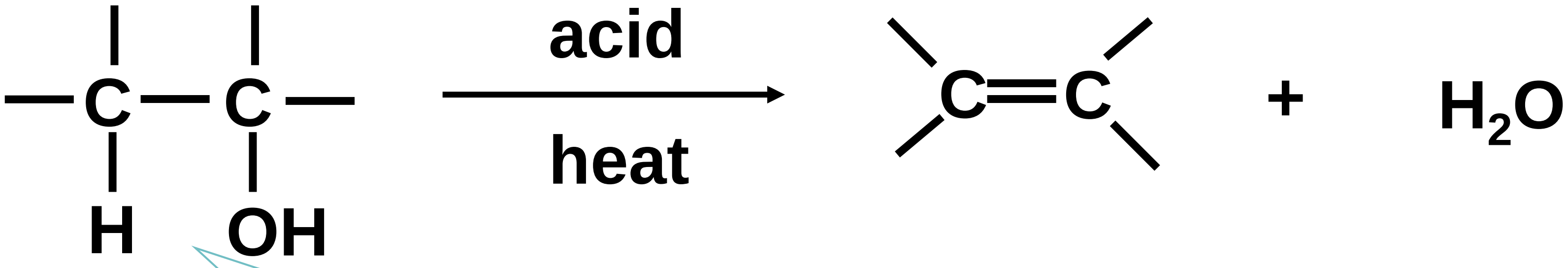
3° alcohol

SUMMARY

Class of alcohol	Reaction with	Product
1^{o}	$KMnO_4$ /$Na_2Cr_2O_7$ / $K_2Cr_2O_7$ / CrO_3	Carboxylic acid
	PCC	Aldehyde
2^{o}	$KMnO_4$ /$Na_2Cr_2O_7$ / $K_2Cr_2O_7$ / CrO_3	Ketone
	PCC	Ketone
3^{o}	$KMnO_4$ /$Na_2Cr_2O_7$ / $K_2Cr_2O_7$ / CrO_3	No reaction
	PCC	

(D) DEHYDRATION

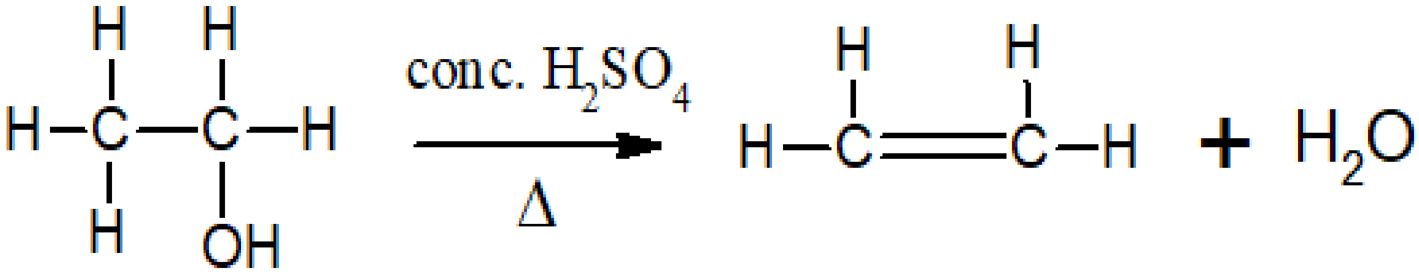
- **Reactant : alcohol**
- **Condition :**
  - **conc. H_2SO_4**
  - **heat**
- **Product : alkene and H_2O**



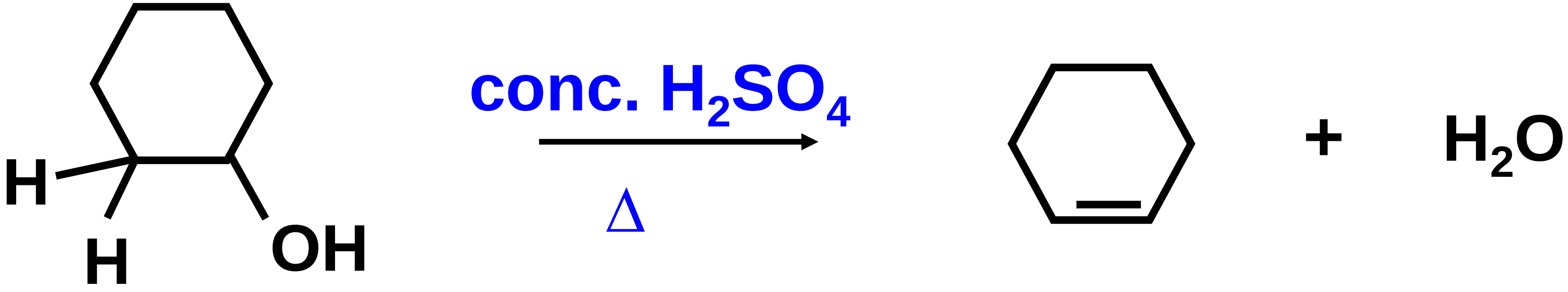
H and OH eliminated!

- **Follow Saytzeff's rule**

EXAMPLE:



ethanol ethene

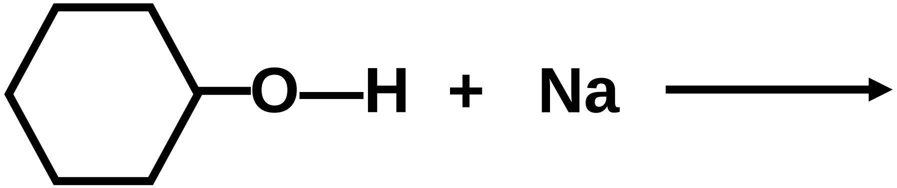


cyclohexanol cyclohexene

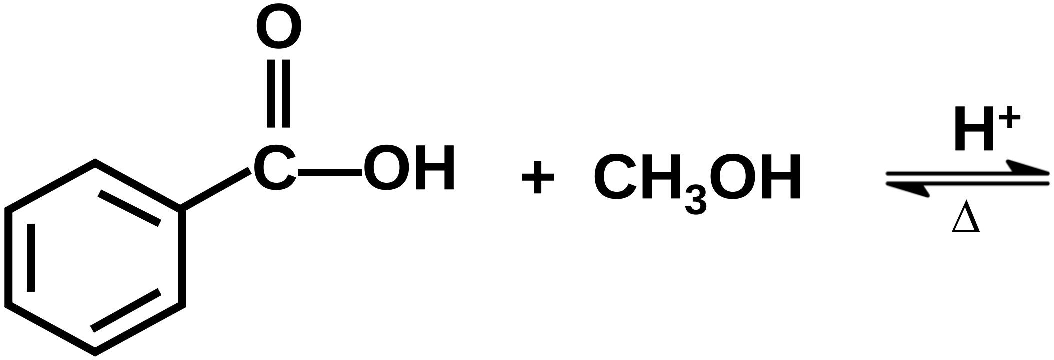
EXERCISE 4

Give the product formed for the following reaction:

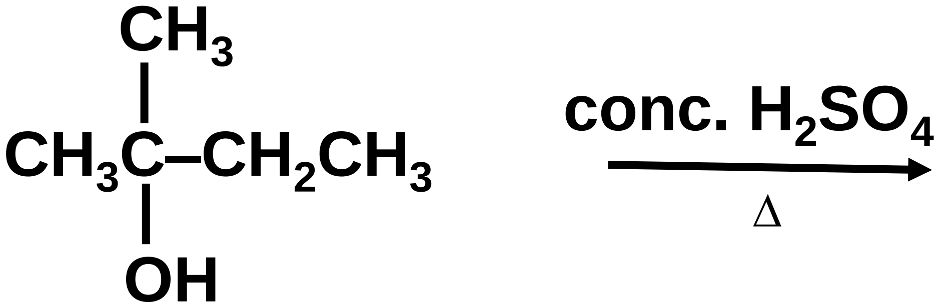
a)



b)



c)



(E) SUBSTITUTION REACTION USING HX, PX_3 , PCl_5 OR $SOCl_2$

- ☐ **ROH reacts with HX, PX_3 , PCl_5 or $SOCl_2$ to produce haloalkane.**

General reaction:

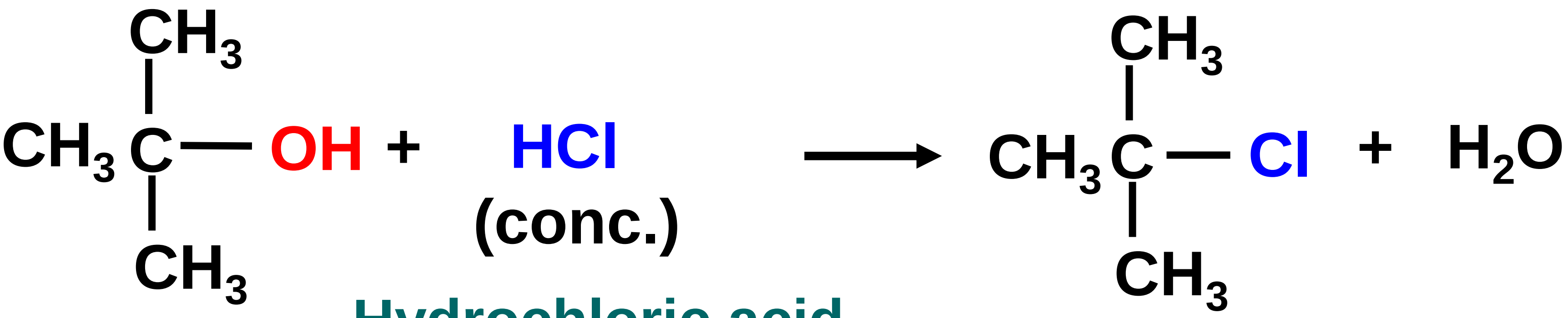
(i) $ROH + HX \longrightarrow RX + H_2O$ (X = Cl, Br)

(ii) $ROH + PX_3 \longrightarrow RX + H_3PO_3$ (X = Cl, Br)

(iii) $ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$

(iv) $ROH + SOCl_2 \longrightarrow RCl + SO_2 + HCl$

EXAMPLE:



$$CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-OH + \underset{\text{(conc.)}}{HCl} \longrightarrow CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-Cl + H_2O$$

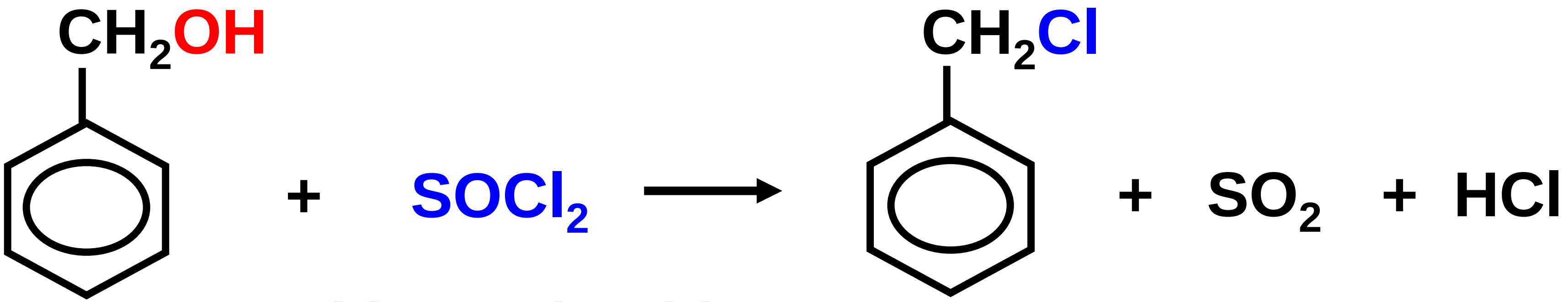
Hydrochloric acid

$(CH_3)_2CHCH_2OH + PBr_3 \longrightarrow (CH_3)_2CHCH_2Br + H_3PO_3$

Phosphorus tribromide

$CH_3CH_2OH \quad + \quad PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$

Phosphorus pentachloride



thionyl chloride

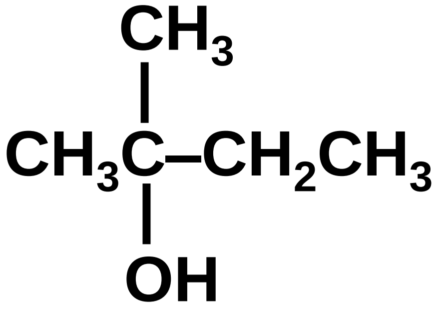
EXERCISE 5:

Give the structures of the products you would expect when 2–methyl–2–butanol reacts with:

a) conc. HCl
b) PBr_3
c) $SOCl_2$

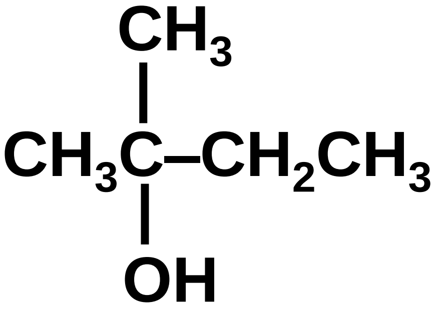
ANSWER:

a)



$$\mathrm{CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}{-}CH_2CH_3} \quad + \quad \text{conc. HCl} \longrightarrow$$

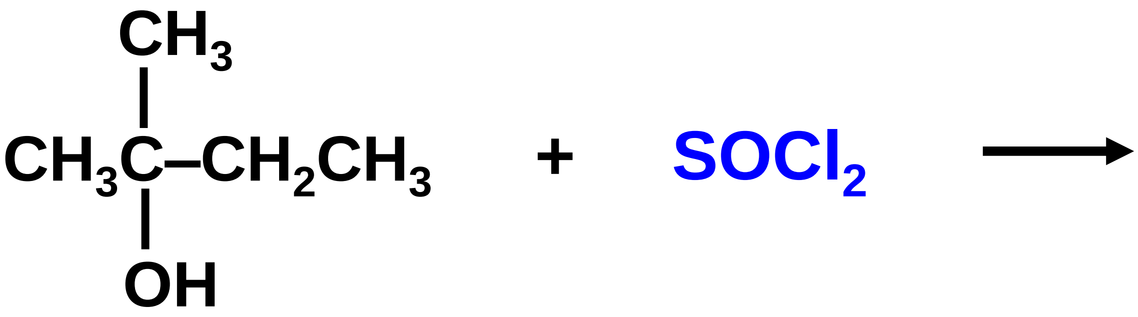
b)



$$\mathrm{CH_3\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}{-}CH_2CH_3} \quad + \mathrm{PBr_3} \quad \longrightarrow$$

ANSWER

c)



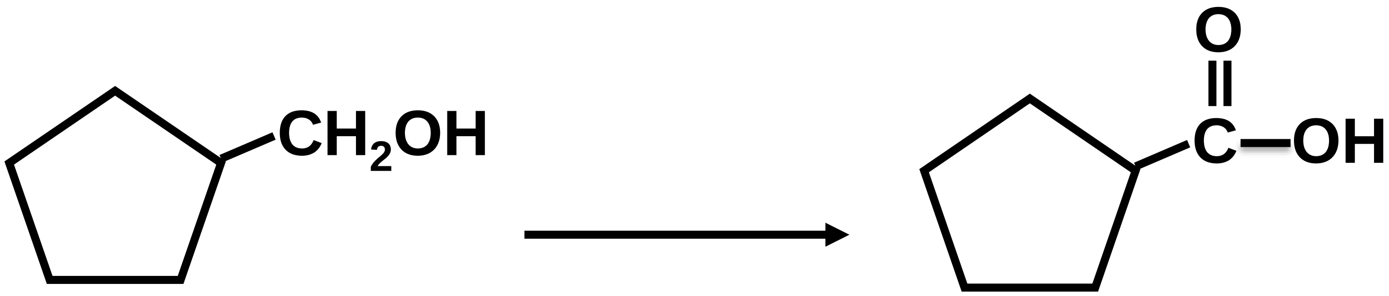
$$CH_3\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_2CH_3 \quad + \quad SOCl_2 \quad \longrightarrow$$

EXERCISE 6

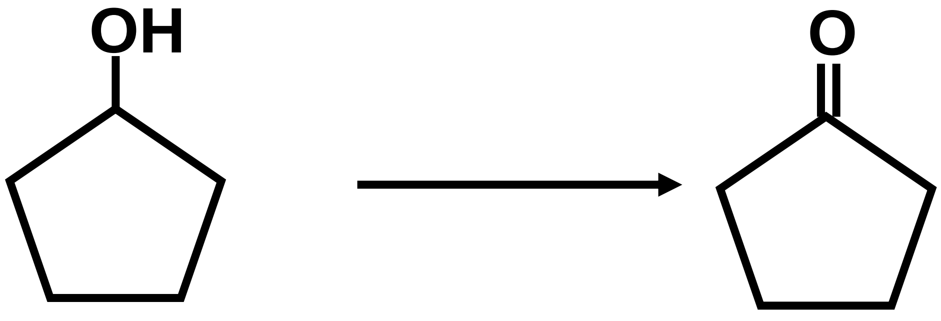
Show how each of the following transformations could be accomplished:

a)

b)



c)



1) LUCAS TEST

- ☐ **Lucas reagent : $HCl_{(conc.)}$ + $ZnCl_2$**

$$R\text{-}OH \xrightarrow{\text{conc. } HCl,\ ZnCl_2} R\text{-}Cl + H_2O$$

TYPE OF ALCOHOL	**OBSERVATION**
1°	**No cloudy solution form at room temperature even after 15 minutes.**
2°	**Cloudy solution formed within 5 - 10 minutes.**
3°	**Cloudy solution formed immediately.**

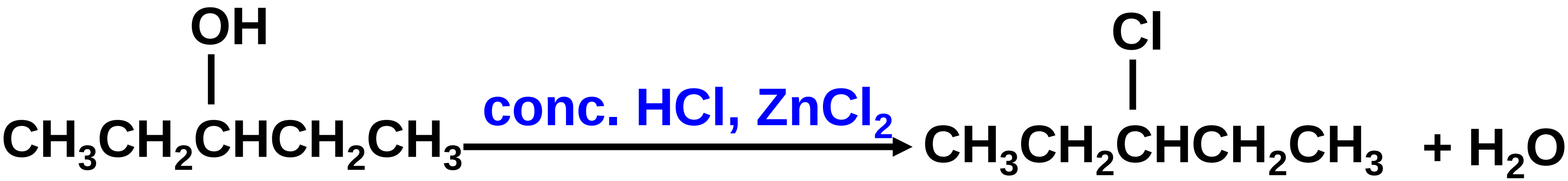
Example :

$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{\text{conc. HCl, ZnCl}_2}$ no observable changes

1–pentanol

(1º alcohol)

OBSERVATION: No cloudy solution form at room temperature even after 15 minutes.



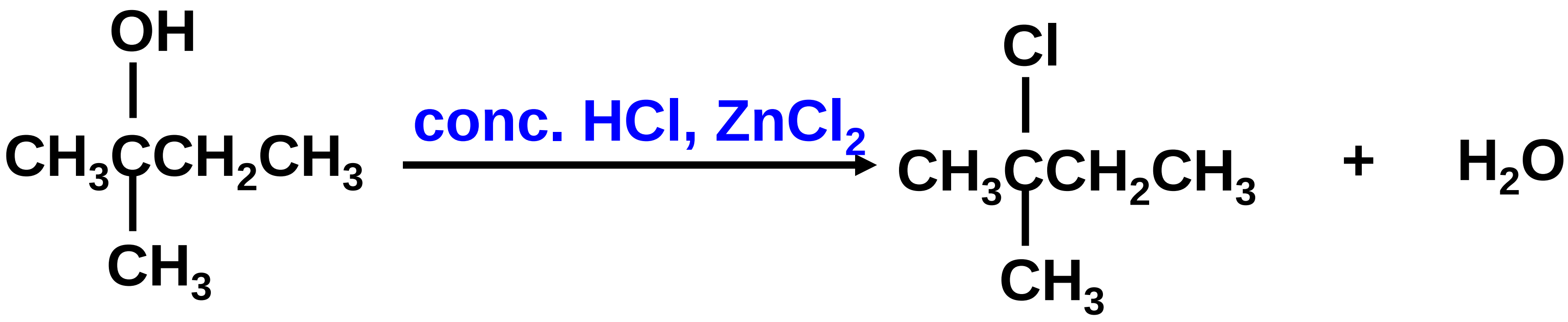
$$CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{\text{conc. HCl, ZnCl}_2} CH_3CH_2\overset{Cl}{\overset{|}{C}}HCH_2CH_3 + H_2O$$

3–pentanol

(2º alcohol)

3–chloropentane

OBSERVATION: Cloudy solution formed within 5 - 10 minutes.



$$CH_3\underset{CH_3}{\overset{OH}{C}}CH_2CH_3 \xrightarrow{\text{conc. HCl, ZnCl}_2} CH_3\underset{CH_3}{\overset{Cl}{C}}CH_2CH_3 \quad + \quad H_2O$$

2–methyl-2-butanol

(3^o alcohol)

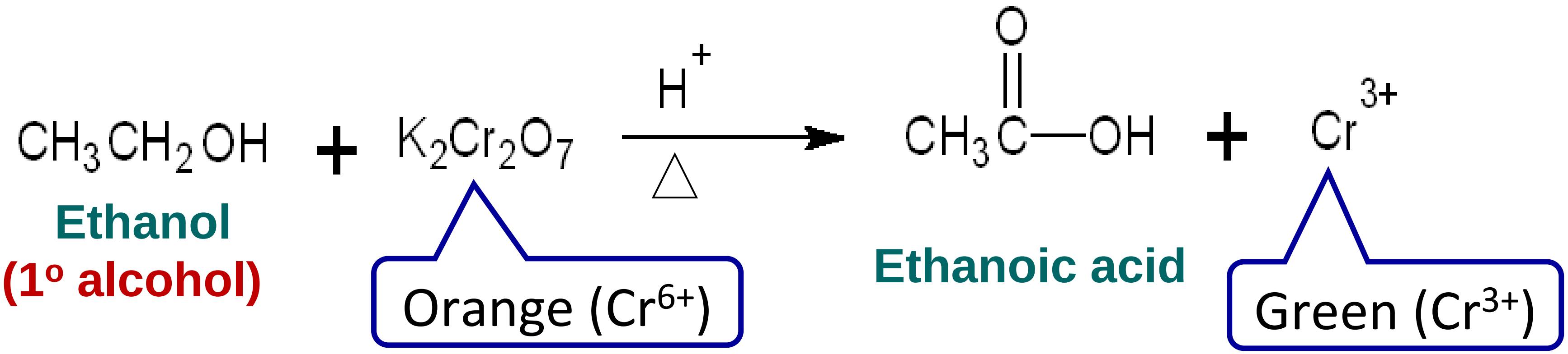
2–chloro-2-methylbutane

OBSERVATION: Cloudy solution formed immediately.

2) OXIDATION TEST

Class of alcohol	Reaction with	Observation
1º	acidified **$K_2Cr_2O_7$ or $Na_2Cr_2O_7$**	**Orange colour of $K_2Cr_2O_7$ turned to green.**
	acidified **$KMnO_4$**	**Purple colour of $KMnO_4$ is decolourised.**
2º	acidified **$K_2Cr_2O_7$ or $Na_2Cr_2O_7$**	**Orange colour of $K_2Cr_2O_7$ turned to green.**
	acidified **$KMnO_4$**	**Purple colour of $KMnO_4$ is decolourised.**
3º	acidified **$K_2Cr_2O_7$ or $Na_2Cr_2O_7$**	**Orange colour of $K_2Cr_2O_7$ remain unchanged.**
	acidified **$KMnO_4$**	**Purple colour of $KMnO_4$ remain unchanged.**

❑ Oxidation using acidified solution of $K_2Cr_2O_7$ or $Na_2Cr_2O_7$ or CrO_3 :



$$CH_3CH_2OH + K_2Cr_2O_7 \xrightarrow[\triangle]{H^+} CH_3\overset{\overset{O}{||}}{C}{-}OH + Cr^{3+}$$

Ethanol

(1^o alcohol)

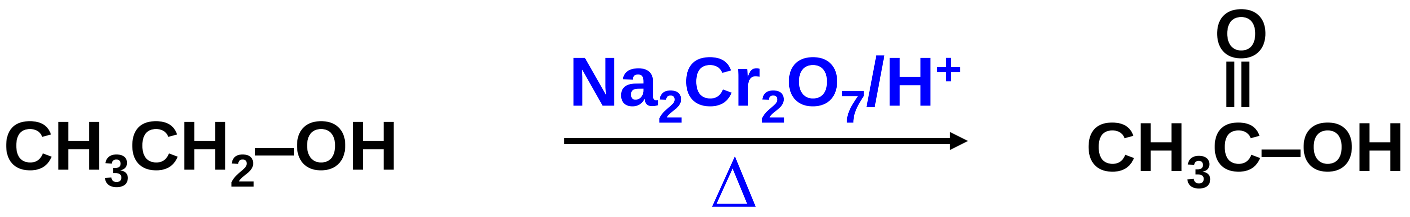
Orange (Cr^{6+})

Ethanoic acid

Green (Cr^{3+})

OBSERVATION: Orange colour of $K_2Cr_2O_7$ turns to green.

Example:



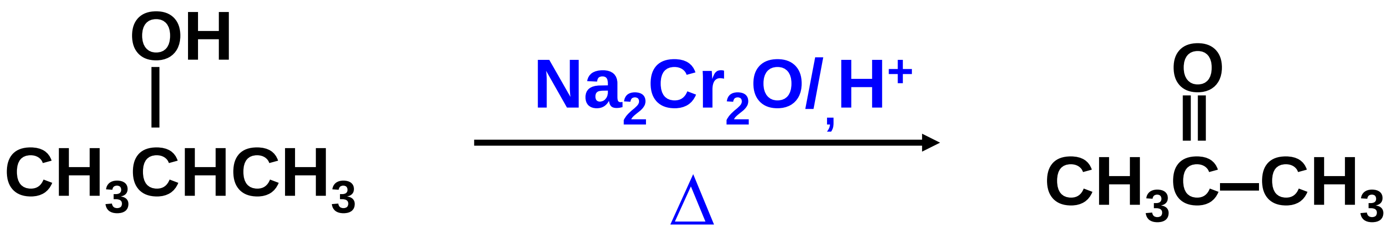
$$CH_3CH_2{-}OH \xrightarrow[\Delta]{Na_2Cr_2O_7/H^+} CH_3\overset{\overset{O}{\|}}{C}{-}OH$$

ethanol

(1º alcohol)

ethanoic acid

OBSERVATION: Orange colour of $Na_2Cr_2O_7$ turns to green.



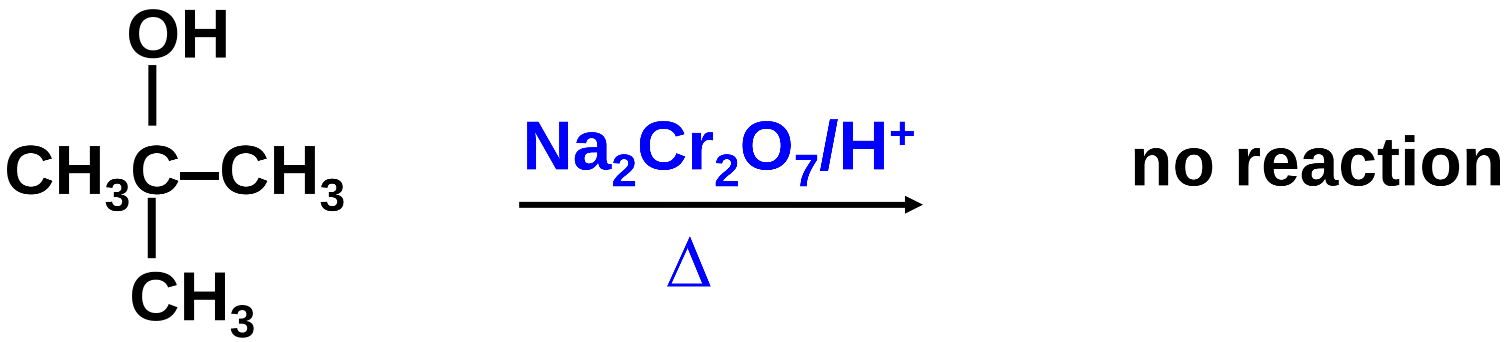
$$CH_3\overset{\overset{OH}{|}}{C}HCH_3 \xrightarrow[\Delta]{Na_2Cr_2O/_{,}H^+} CH_3\overset{\overset{O}{\|}}{C}{-}CH_3$$

2–propanol

(2º alcohol)

propanone

OBSERVATION: Orange colour of $Na_2Cr_2O_7$ turns to green.



$$CH_3\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!-\!CH_3 \xrightarrow[\Delta]{Na_2Cr_2O_7/H^+} \text{no reaction}$$

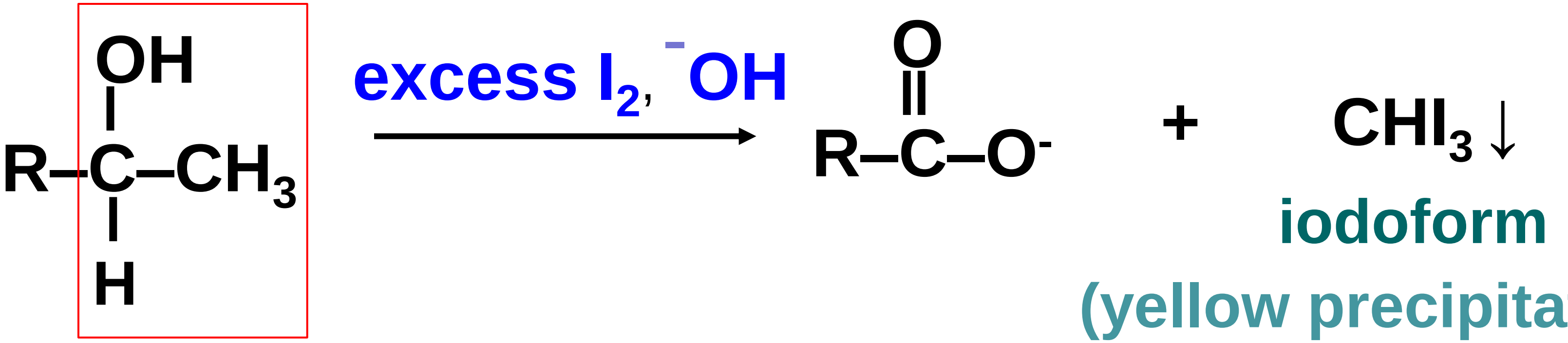
2–methyl-2–propanol

(3º alcohol)

OBSERVATION: Orange color of $Na_2Cr_2O_7$ remain unchanged.

3) IODOFORM TEST

- To detect **methyl carbinol** group.
- Reagent: excess I_2 , NaOH (base)
- Methyl carbinol cleavage to give **carboxylate ion** and **iodoform**.



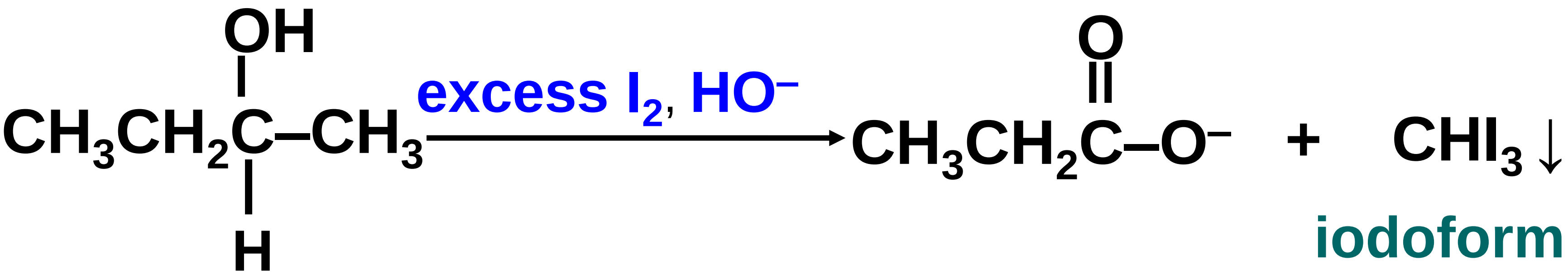
$$R-\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}-CH_3 \xrightarrow{\text{excess } I_2,\ {}^{-}OH} R-\overset{\overset{O}{\|}}{C}-O^- \quad + \quad CHI_3\downarrow$$

iodoform

(yellow precipitate)

OBSERVATION: Light yellow precipitate formed.

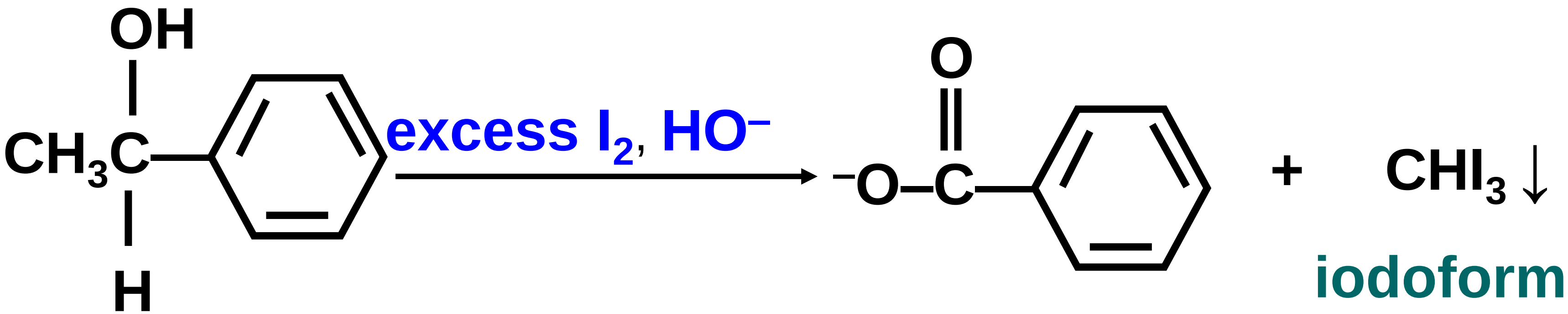
Example:



$$CH_3CH_2\overset{OH}{\underset{H}{C}}-CH_3 \xrightarrow{\text{excess } I_2,\ HO^-} CH_3CH_2\overset{O}{\overset{\|}{C}}-O^- \quad + \quad CHI_3\downarrow$$

iodoform

OBSERVATION: Light yellow precipitate formed.



OBSERVATION: Light yellow precipitate formed.

EXERCISE 7:

Show how you would use a simple test to distinguish between the following pairs of compounds. Tell what you would observe with each compound. Write the chemical equation involved.

(a) 1–hexanol and cyclohexanol
(b) 2-butanol and 3-pentanol
(c) 2–butanol and 1–methylcyclohexanol

ANSWER :

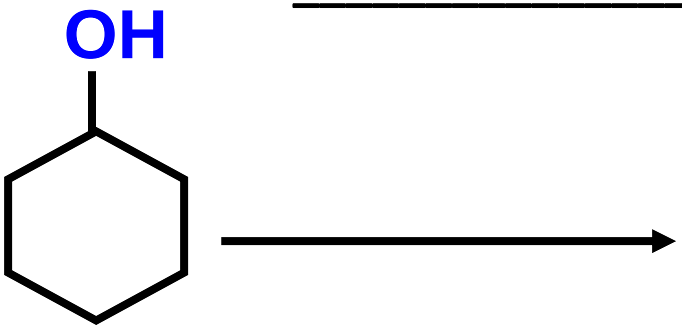
(a) 1–hexanol and cyclohexanol

Test:__________________

$CH_3CH_2CH_2CH_2CH_2CH_2OH \longrightarrow$

OBSERVATION: ____

____



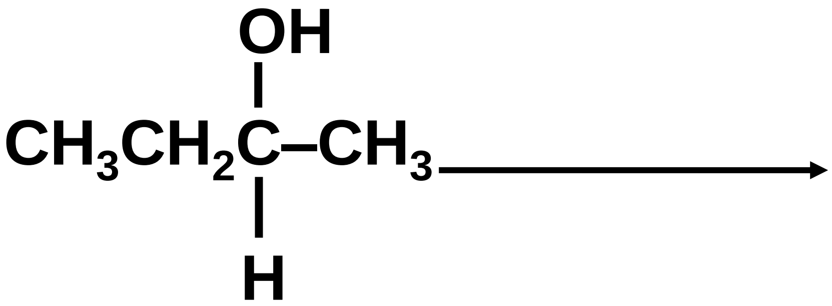
OBSERVATION: ____

____

ANSWER :

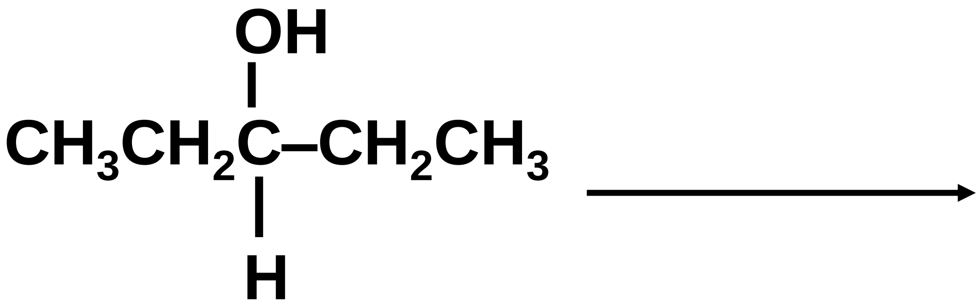
(b) 2-butanol and 3-pentanol

Test:______________________



$$CH_3CH_2\overset{OH}{\underset{H}{C}}-CH_3 \longrightarrow$$

OBSERVATION: ______________________________________



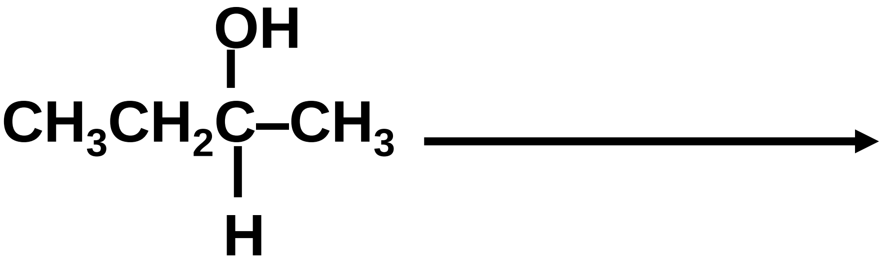
$$CH_3CH_2\overset{OH}{\underset{H}{C}}-CH_2CH_3 \longrightarrow$$

OBSERVATION: ______________________________________

ANSWER:

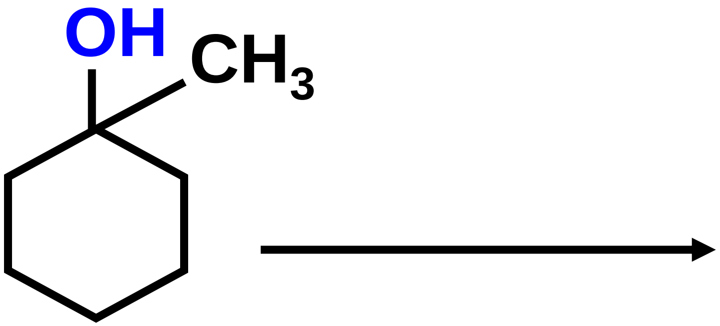
(c) 2–butanol and 1–methylcyclohexanol

Test: ____________________



$$CH_3CH_2\overset{OH}{\underset{H}{C}}-CH_3 \longrightarrow$$

OBSERVATION: ____



OBSERVATION: ____

8.5 LEARNING OUTCOMES

Phenol

a) Compare the acidity of phenol, alcohol and water (C4)

b) Explain the chemical properties of phenol with reference to: (C3,C4)
    i. Reaction with sodium
    ii. Reaction with sodium hydroxide
    iii. Identification tests using
        -$FeCl_3$ solution and
        -bromine water

8.5

PHENOL

- Phenol
  - Acidity of phenol
    - **Compare the acidity of phenol, alcohol and water**
  - Chemical Properties of Phenol
    - **Reaction with sodium**
    - **Reaction with sodium hydroxide**
    - **Identification test using:**
      - **Bromine water**
      - **$FeCl_3$**

ACIDITY OF PHENOL, ALCOHOL AND WATER

- **Alcohol, water and phenol have different acidity (different K_a values).**
- **Acidity increases in the order of :**

Alcohol (aliphatic alcohol) < water < phenol

- Like water, both alcohol and phenol are **weakly acidic.**
  - As weak acid (donate H^+):

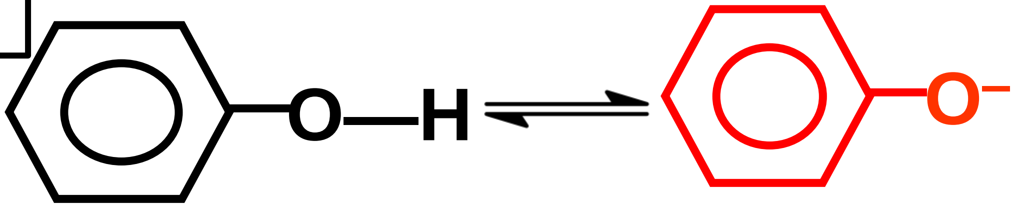
Water $\quad H—O—H \rightleftharpoons H—O^- + H^+$

hydoxide ion $\quad (Ka \approx 10^{-14})$

Alcohol $\quad R—O—H \rightleftharpoons R—O^- + H^+$

alkoxide ion $\quad (K_a \approx 10^{-16})$

Phenol



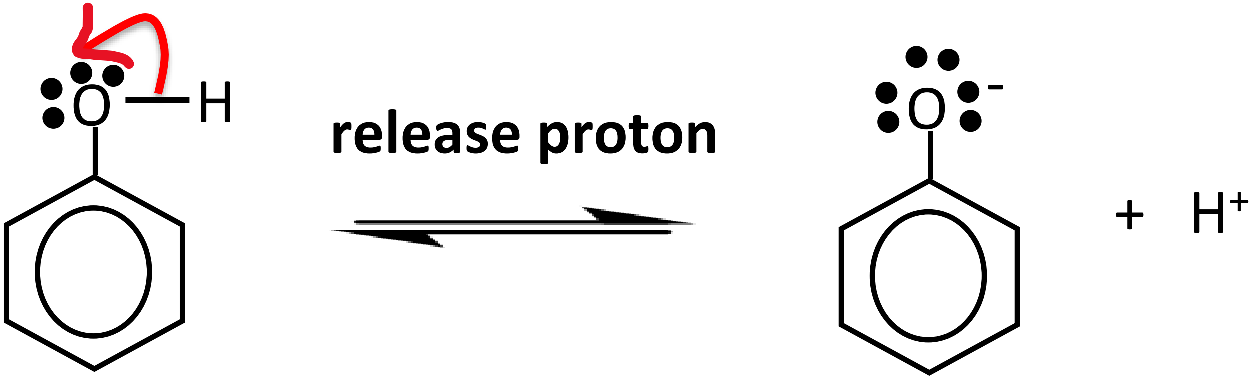
$+ H^+$

$(K_a \approx 10^{-10})$

phenoxide ion

Alcohol(aliphatic alcohol) < Water < Phenol

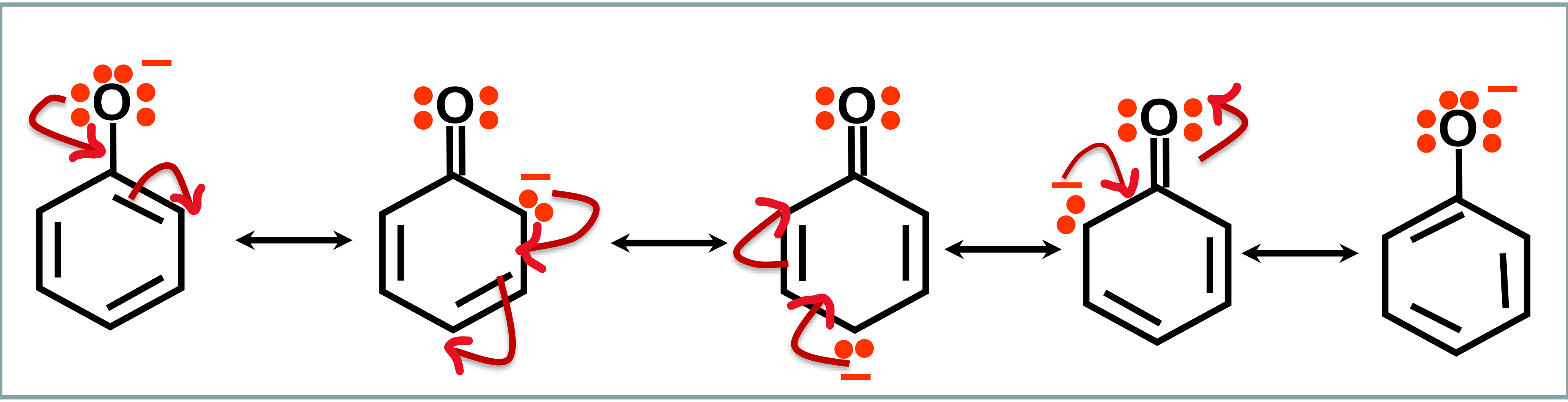
- **Phenol more acidic than aliphatic alcohol and water.**
  - **due to phenoxide ion formed is more stable than the alkoxide ion (from alcohol) and hydroxide ions (from water).**



phenoxide ion

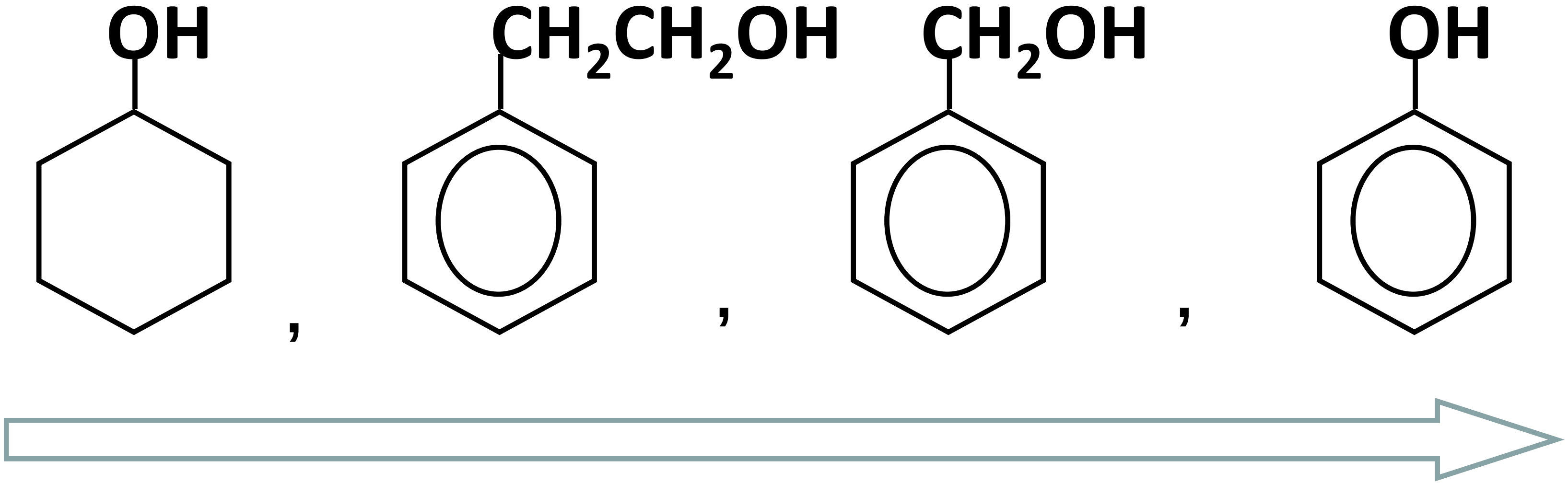
- The phenoxide ion formed is stabilised by **resonance effect.**

RESONANCE–STABILIZED PHENOXIDE ION



- The ability to spread the negative charge over four atoms rather than concentrated it on just one atom produces more stable ion.

Example:



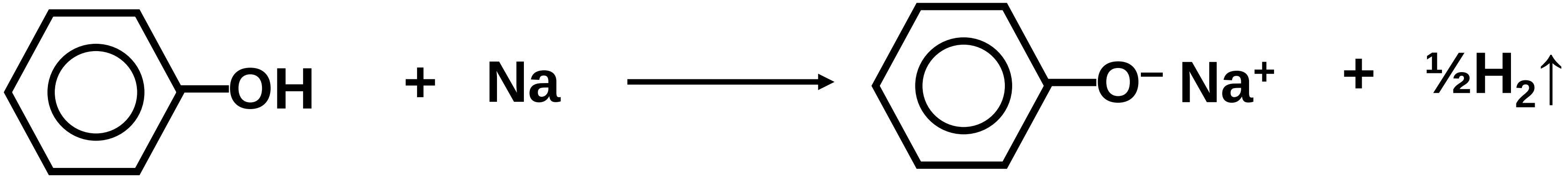
Acidity increase

CHEMICAL PROPERTIES OF PHENOL

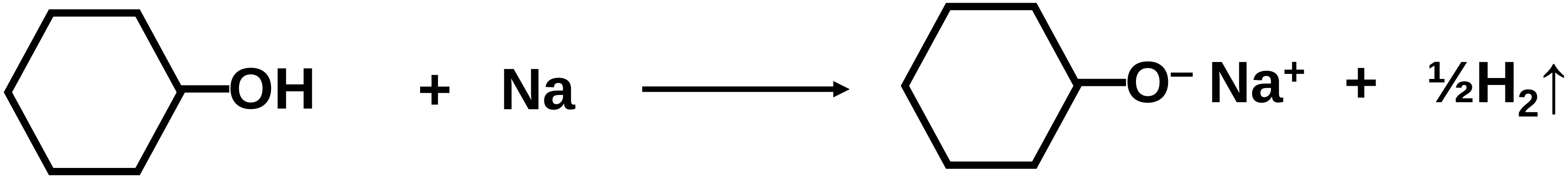
1) Reaction with Na

- Both alcohols and phenols can react with Na.

EXAMPLE:



phenol



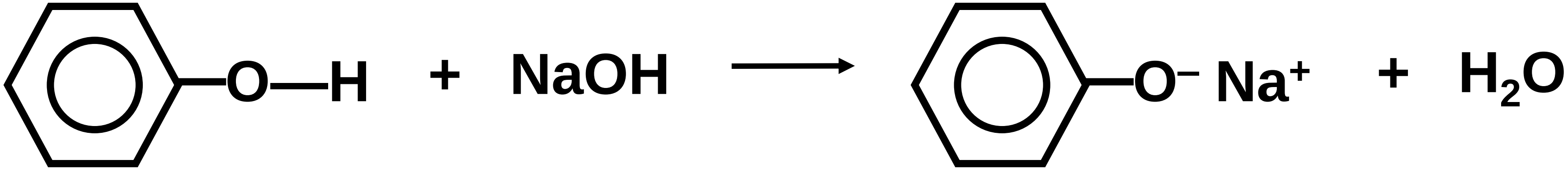
cyclohexanol

2) Reaction with NaOH

- ❑Phenols are soluble in aqueous NaOH but alcohols with six C atom or more do not.

- ❑ Phenols are much more acidic than alcohols.

EXAMPLE:



phenol

sodium phenoxide

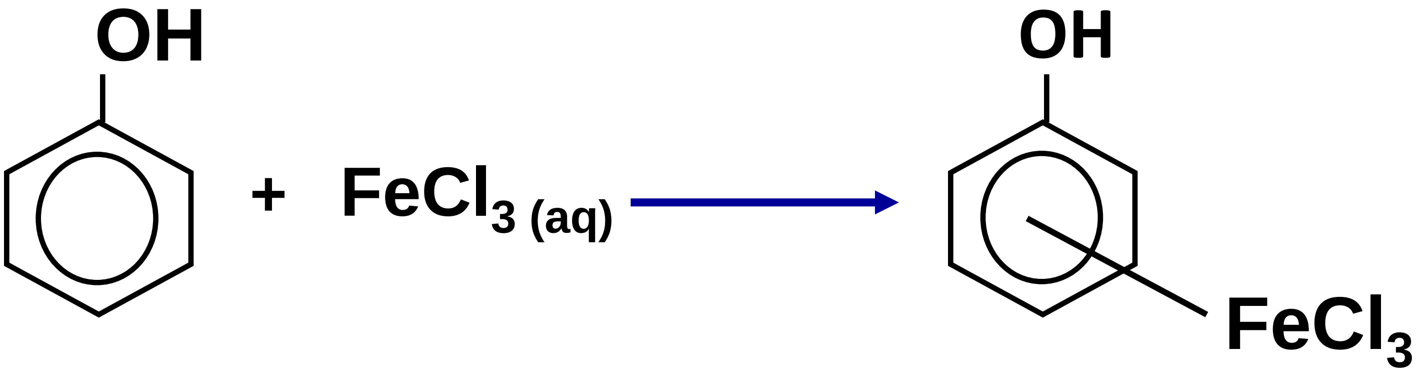
$CH_3(CH_2)_4CH_2OH$ + NaOH ⟶ almost insoluble

1–hexanol

IDENTIFICATION TEST

1) Using $FeCl_3$ solution

- ❑ Phenol reacts with aqueous solution of iron (III) chloride to form a purple complex.

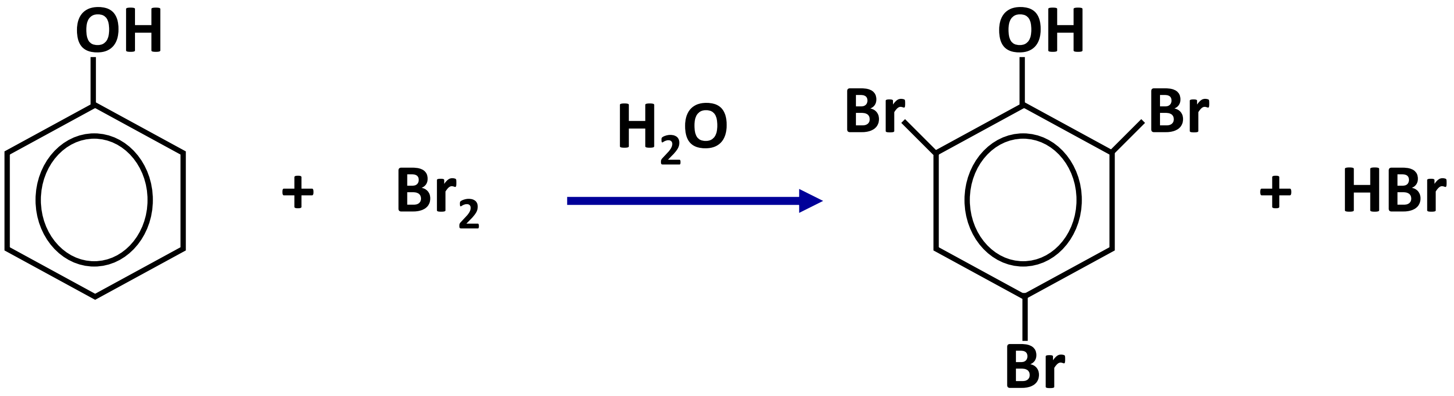


Purple complex

OBSERVATION: Purple complex formed.

2) Using bromine water

- Phenol reacts with aqueous bromine to form white precipitate.



2,4,6-tribromophenol

White precipitate

OBSERVATION: White precipitate formed.

GLOSSARY

1. Alcohol – organic compounds containing hydroxyl functional group.
2. Esterification – reaction between carboxylic acid and alcohol to produce ester and water.
3. Oxidation – loses a bond to hydrogen and gains a new bond to oxygen.
4. Lucas test – use of concentrated hydrochloric acid and anhydrous zinc chloride to identify classes of alcohols.
5. Iodoform test – use of excess iodine and sodium hydroxide to detect the presence of methyl carbinol and methyl carbonyl group