



Chem 145

Alcohols and Phenols

Chapter 7

1434-1435
2013-2014
2nd semester

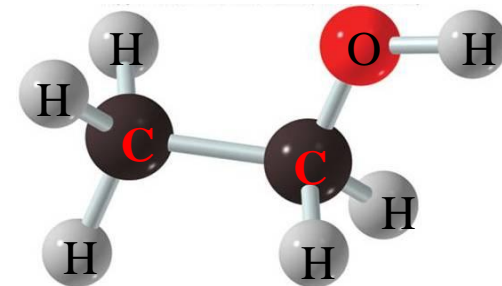
Dr. Seham ALTERARY

Chapter Head Lines

- ▶ Introduction
- ▶ Types and Classifications.
- ▶ Nomenclature of Alcohols and Phenols.
- ▶ Physical Properties.
- ▶ Acidity of Alcohols and Phenols.
- ▶ Preparation of Alcohols and Phenols:
 - A. Preparation of Alcohols
 - 1- Hydration of Alkyl halide
 - 2- Hydration of Alkenes
 - 3- Oxidation of Alkenes to vicinal diol.
 - 4- Reduction of Carbonyl group.
 - 5- Nucleophilic Addition of Grignard Reagents to carbonyl group
 - B. Preparation of Phenols
- ▶ Reactions of Alcohols and Phenols:
 - I- Reactions involving **oxygen-hydrogen** bond breaking
 - II- Reactions involving **carbon-oxygen** bond rupturing
 - III. Oxidation
 - IV- Reaction of Aromatic Ring of Phenols

Introduction

Alcohols

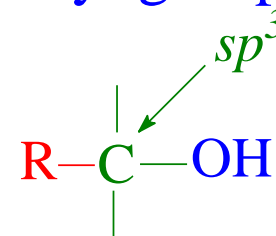


-Alcohols are characterized by *the hydroxyl group* -OH

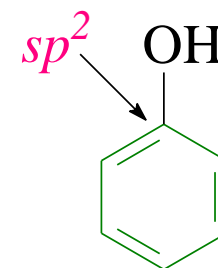
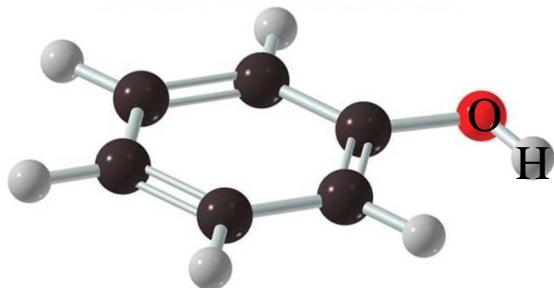
-The general formula for Alcohols is

As all alcohols are the compounds containing hydroxyl group (-OH) attached to the alkyl group, hybridization is sp^3

Phenols or, Aryl alcohols



- Are hydroxyl derivatives of aromatic hydrocarbons, which are derived by replacing hydrogen atom attached to sp^2 hybridized carbon atom(s) of benzene ring by hydroxyl group.



Phenols , ArOH

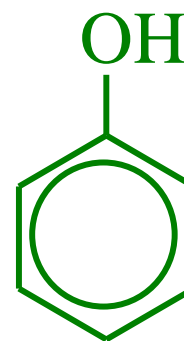
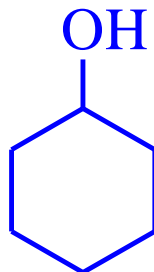
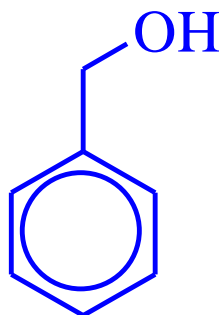
Alcohols and phenols have a common functional group
the hydroxyl group, —OH.

Alcohols and phenols may be viewed as organic derivatives of water.

H-O-H
Water

R-O-H or PhCH₂OH
Alcohol

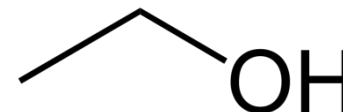
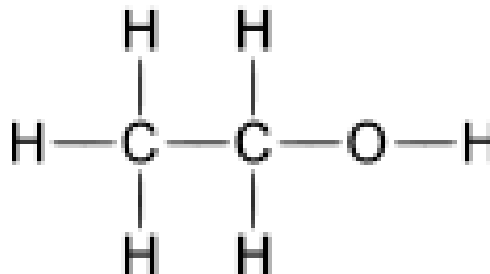
Ph-O-H
Phenol



Types of Alcohols

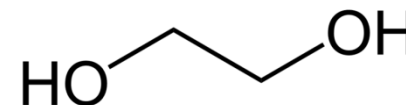
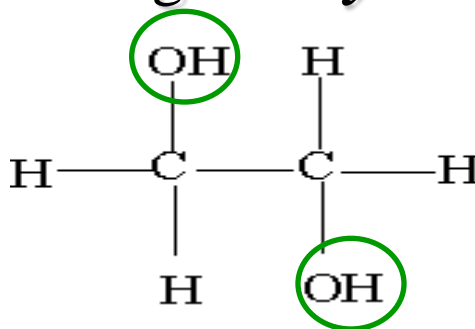
1. Monohydroxyls: containing **one hydroxyl group**.

Example; ethanol ($\text{C}_2\text{H}_5\text{OH}$)



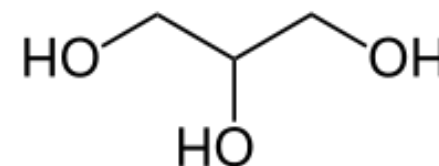
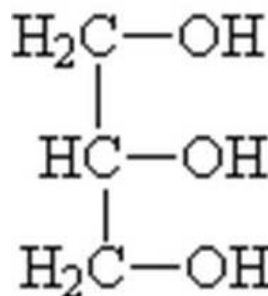
2. Dihydroxyls (glycols): containing **two hydroxyl groups** connected by **different** carbon atoms.

Example; 1,2-Ethanediol
Ethylene glycol
($\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$).



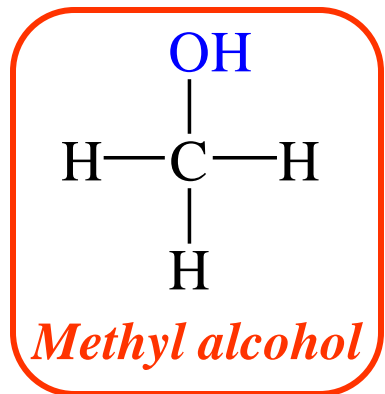
3. Polyhydroxyls: containing **more than two hydroxyl groups** on **different** carbon atoms.

Example; 1,2,3-propanetriol
Glycerol or Glycerin
($\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$).

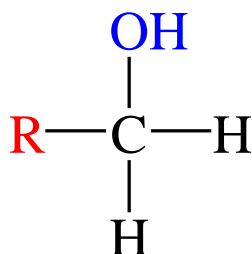


Classification of Monohydroxyl Alcohols

➤ *The mono hydroxyl alcohols* can be classified into three types according to the type of the carbon atom connected to the hydroxyl group:

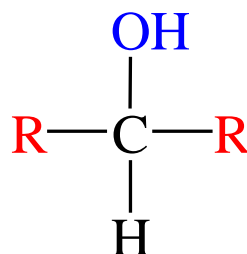


Examples



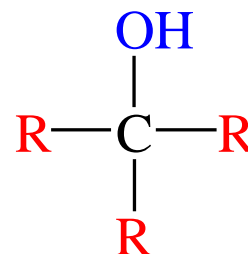
1° alcohol

Ethanol



2° alcohol

2-Propanol



3° alcohol

2-Methyl-2-Propanol

Draw the structures of the above alcohols?

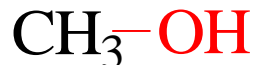
Nomenclature

- You can use both **the common** and **IUPAC systems** to name **alcohols**.

1) Common Nomenclature (Alkyl + alcohol)

- In ***the common system***, you **name an alcohol** by listing **the alkyl group** and adding the word ***alcohol***.

Examples:



Methyl alcohol

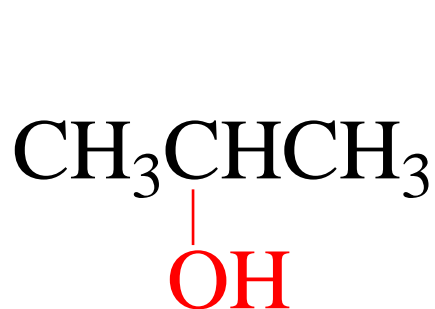


Ethyl alcohol

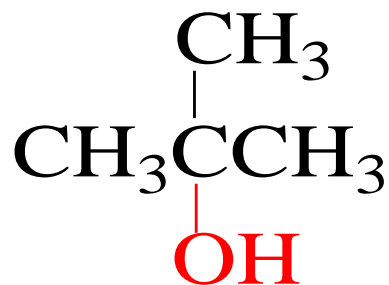


Propyl alcohol

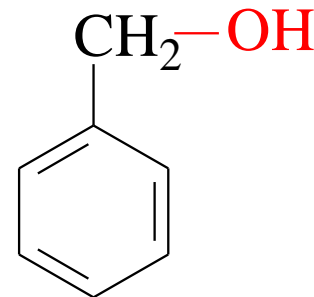
Examples:



Isopropyl **alcohol**



t-butyl **alcohol**



Benzyl **alcohol**



Vinyl **alcohol**



Allyl **alcohol**

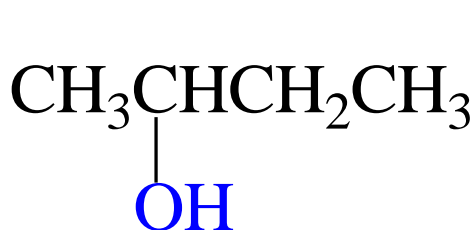
2) IUPAC Nomenclature

- 1) Select the **longest continuous carbon** chain *to which the hydroxyl is directly attached*.
- 2) Change the name of the **alkane** corresponding to this chain by dropping the final **-e** and adding the suffix **-ol**.
- 3) **Number** the longest continuous carbon chain so as to give the carbon atom bearing the **hydroxyl group** the lower number.

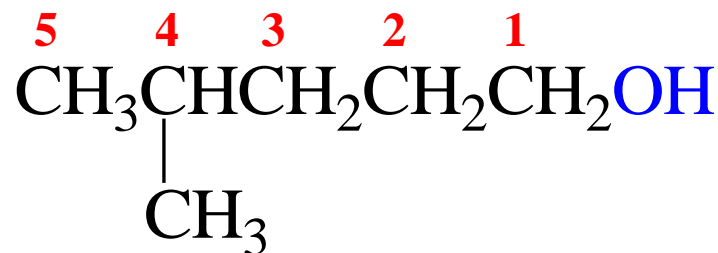
Examples



n-Propanol



2-Butanol

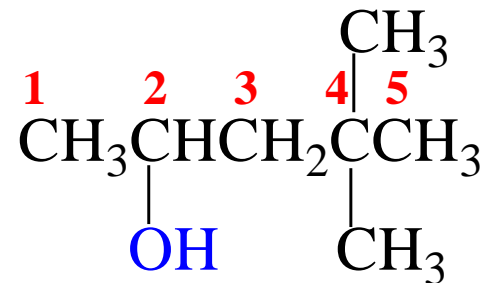


4-Methylpentan-1-ol

Not 2-Methylpentan-5-ol

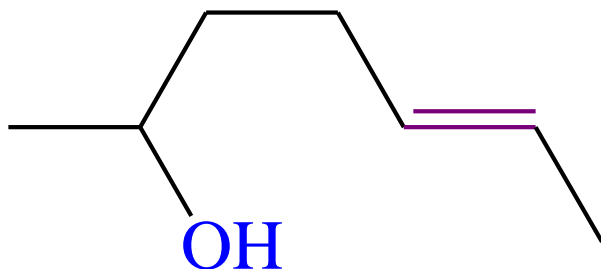


3-chloropropan-1-ol



4,4-Dimethylpentan-2-ol

4) OH group is **preferred over** the double or triple bond in numbering.



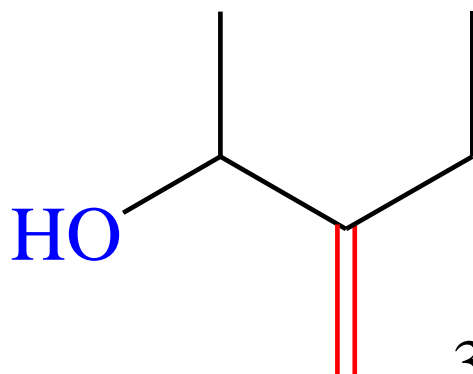
Hept-5-en-2-ol



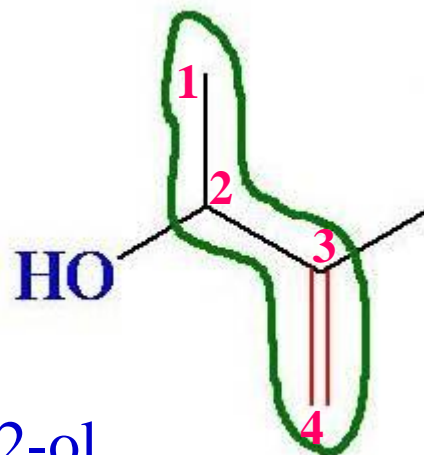
But-3-yn-1-ol

5) If a compound contains both **OH** and a **double** or **triple bond**, choose the chain that *include them both* even if this is **not the longest chain**.

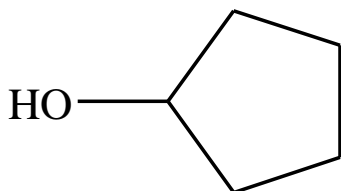
Example



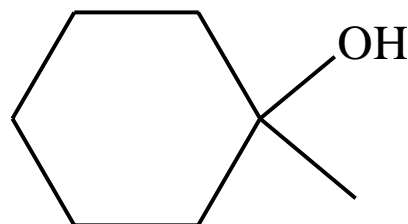
3-Ethylbut-3-en-2-ol



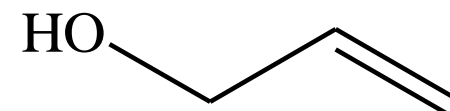
Example



HO



OH

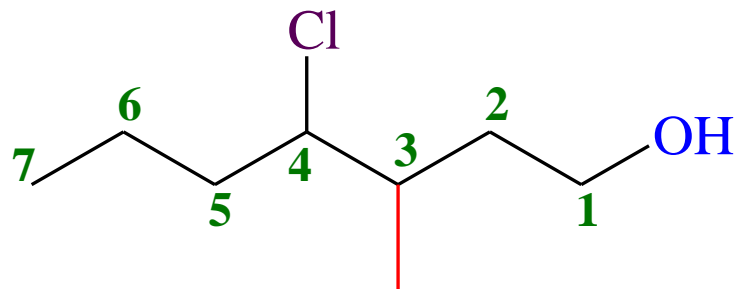


HO

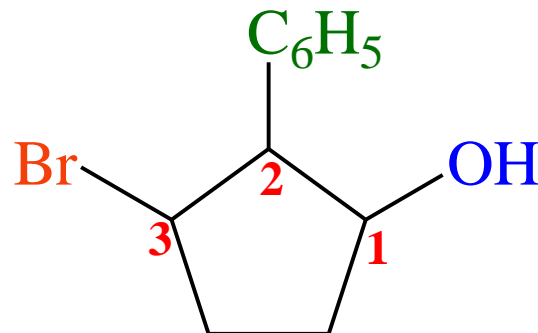
Common: Cyclopentylalcohol Methylcyclohexylalcohol Allyl alcohol

IUPAC: Cyclopentanol 1-Methyl-1-cyclohexanol 2-Propen-1-ol

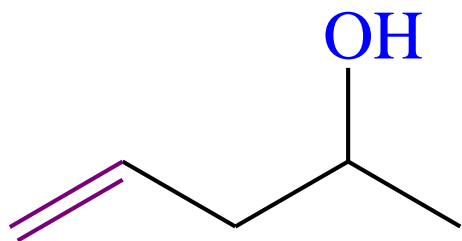
Examples



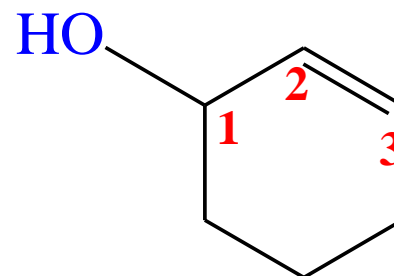
4-Chloro-3-methyl-heptan-1-ol



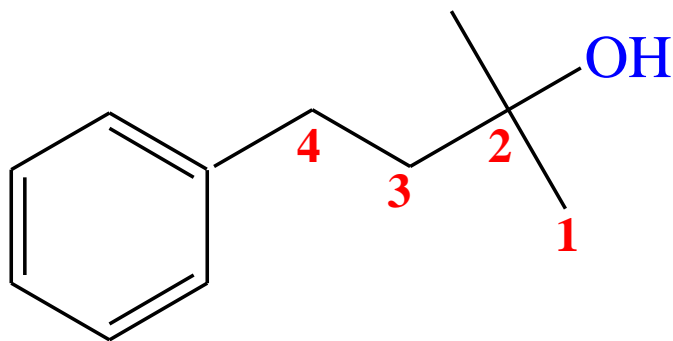
3-Bromo-2-phenyl cyclopentanol



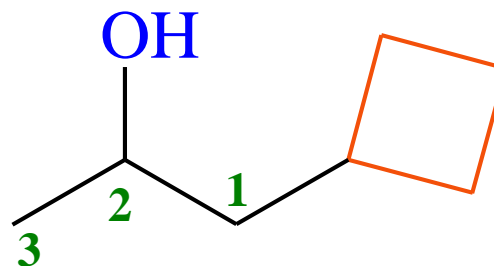
Pent-4-ene-2-ol



Cyclohex-2-enol

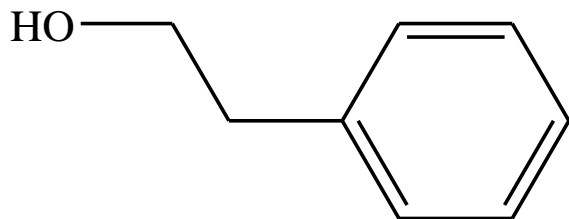


2-Methyl-4-phenyl butan-2-ol

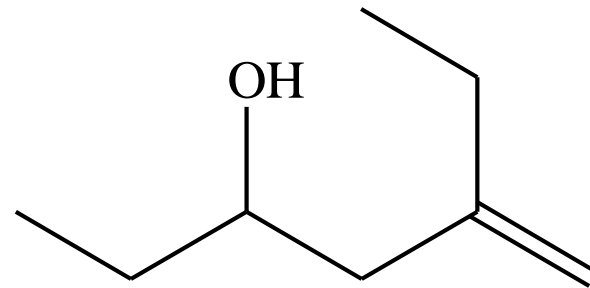


1-Cyclobutylpropan-2-ol

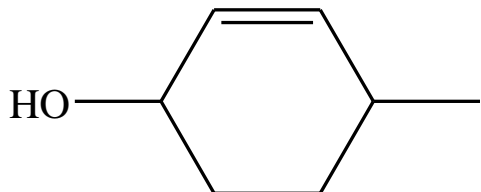
Examples



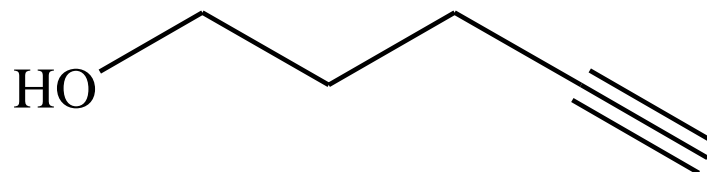
2-phenyl ethanol



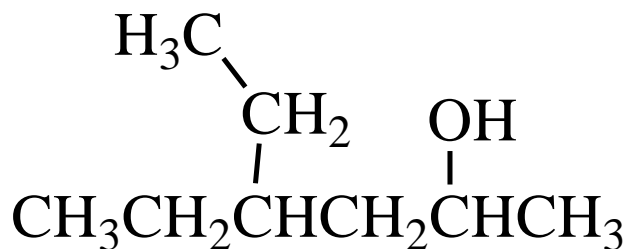
5-Ethyl-hex-5-en-3-ol



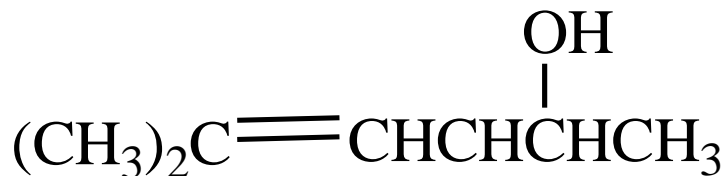
4-methyl-2-cyclohexen-1-ol



pent-4-yn-1-ol



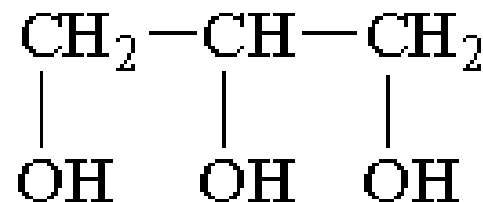
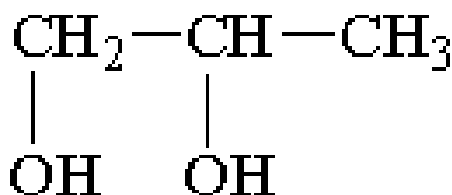
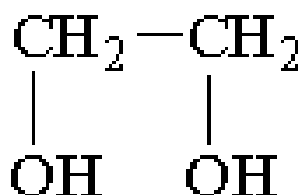
4-Ethyl-hexan-2-ol



5-Methyl-4-hexen-2-ol

- In the IUPAC system, the suffix **diol** is added to the name of the parent hydrocarbon when **two hydroxyl groups** are present, and the suffix **triol** is added when there are **three OH** groups.
- Common names, **two OH groups** on adjacent carbons are known as **1,2-glycols**.

Examples:



IUPAC: **1,2-Ethandiol**

1,2-Propanediol

1,2,3-Propanetriol

Common: **Ethylene glycol**

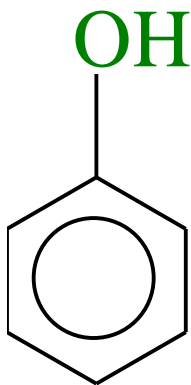
propylene glycol

glycerol or glycerin

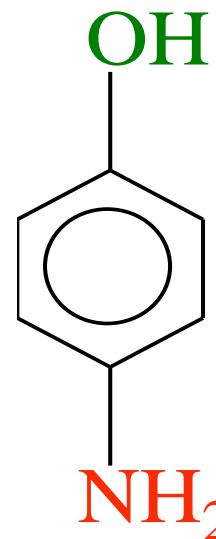
Nomenclature of Phenols

- Compounds that have a **hydroxyl group** attached directly to a **benzene ring** are called **phenols**.
- The **ortho**, **meta**, **para** system is **used in common** names.
- While the numbering system is employed in IUPAC names and in this case numbering of the ring begins at the hydroxyl-substituted carbon and proceeds in **the direction of the next substituted carbon that possesses the lower number**.

Examples:

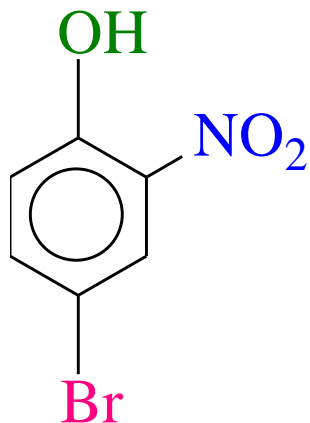


Phenol

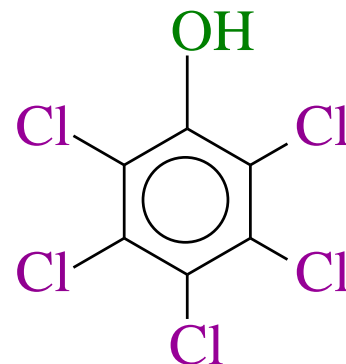


4- Aminophenol

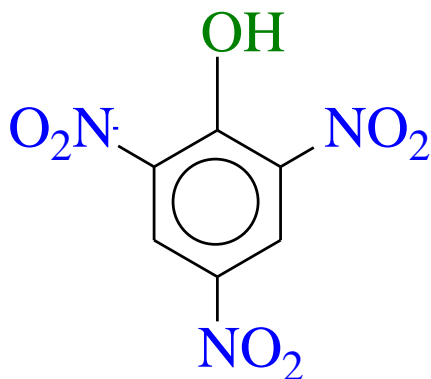
Examples:



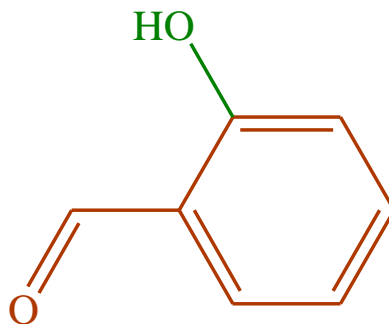
4-Bromo-2-nitrophenol



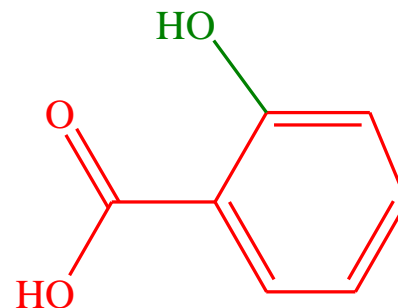
2,3,4,5,6-Pentachlorophenol



2,4,6-Trinitrophenol



2-hydroxybenzaldehyde
***o*-hydroxybenzaldehyde**



2-hydroxybenzoic acid
***o*-hydroxybenzoic acid**

Common name: Picric acid

Salicylaldehyde

Salicylic acid

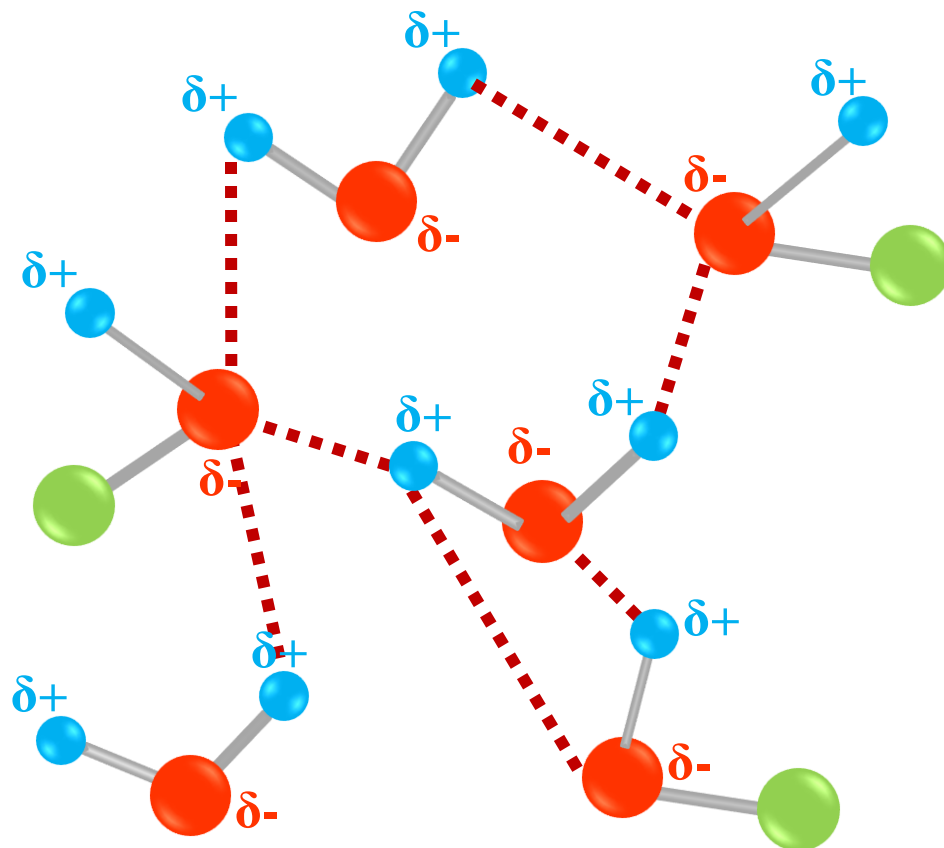
Physical Properties of Alcohols & Phenols

1. Solubility

• Alcohols

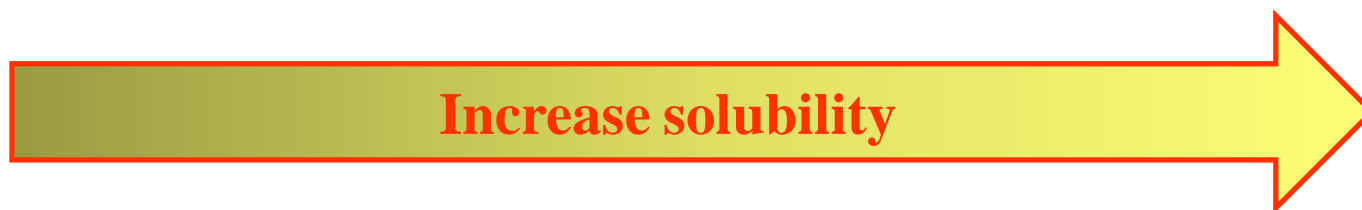
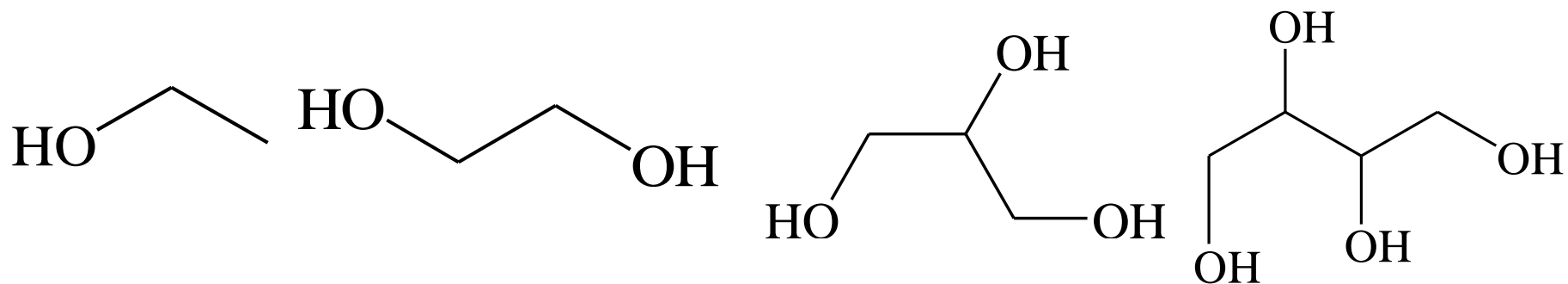
•The first three members are completely **miscible** with **water**. The solubility rapidly **decreases** with **increase in molecular mass**. The **higher members** are almost **insoluble** in **water** but are soluble in organic solvents like **benzene**, **ether** etc.

•The solubility of lower alcohols is due to the existence of **hydrogen bonds** between **water** and **polar -OH group** of alcohol molecules.

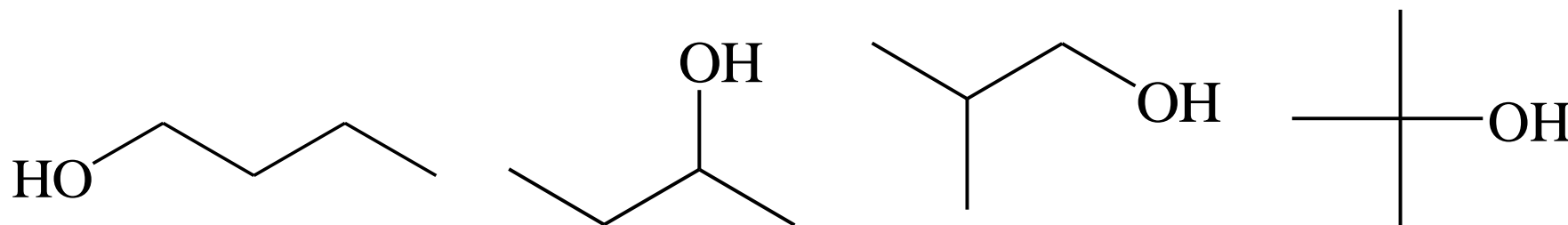


Hydrogen bonding between alcohols and water molecules

- The number of **hydroxyl groups** increases the solubility.



- The solubility **increases** with **branching of chain**.

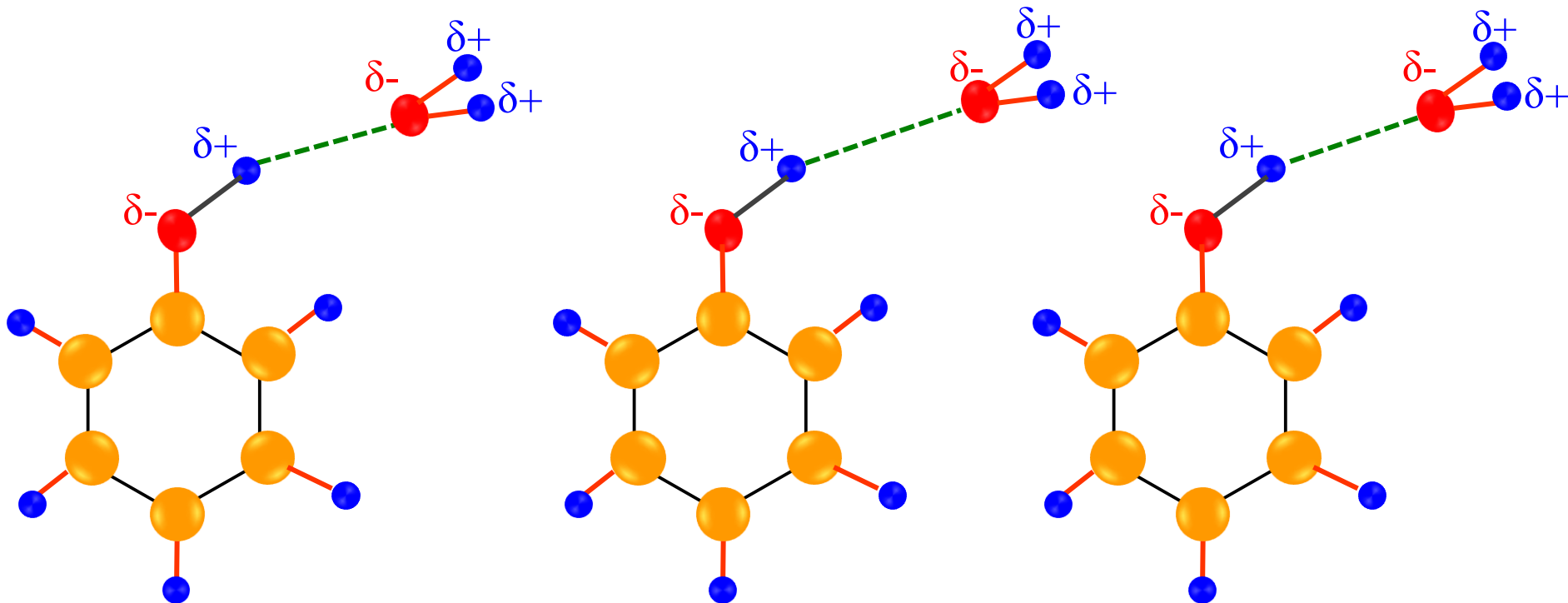


- **Phenols**

Phenols differ from alcohols in that the **-OH** is *directly* attached to the **aromatic ring**.

- Phenols are sparingly soluble in water but readily soluble in organic solvents .

- The **-OH group** in phenols contain a hydrogen bonded to an electronegative oxygen atom. Thus they form hydrogen bonds with water molecules



3. Boiling points

- Alcohols

Boiling points of alcohol increases in regular manner with increase in molecular weight.

Boiling point of alcohols are much higher than those of alkanes, halo alkanes or ethers of comparable molecular masses.



Ethanol

Mol wt = 46; bp= 78°C



n-propane

Mol wt = 44; bp= -42°C

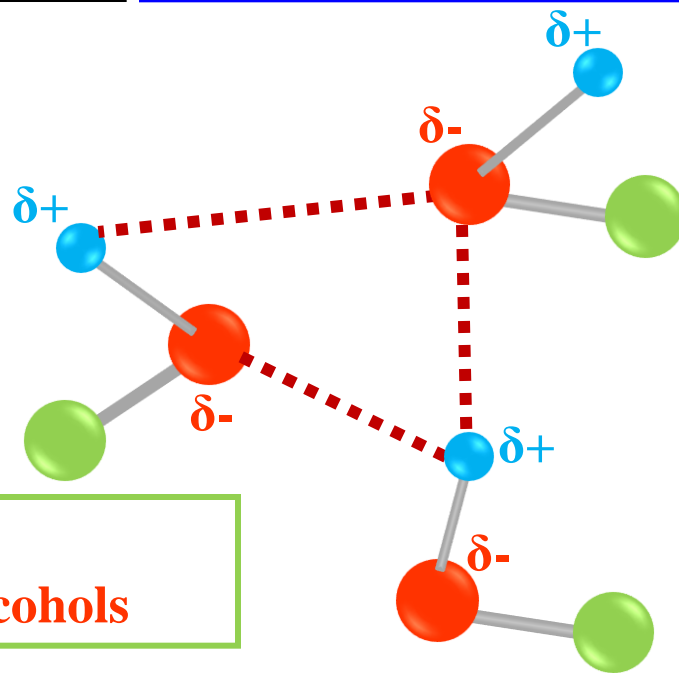


Dimethylether

Mol wt = 46; bp= -24°C

•This is because in alcohols intermolecular hydrogen bonding exists due to which a large amount of energy is required to break these bonds.

Representations of
intermolecular hydrogen bonding in alcohols

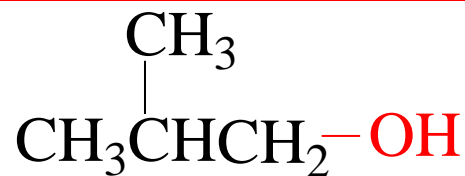


- Among isomeric alcohols, the boiling point decreases with increase in branching in the alkyl group.



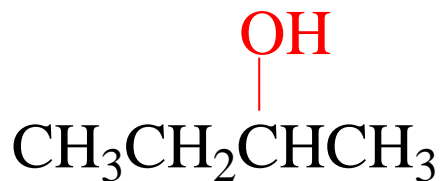
1-Butanol

(mol wt = 74; bp = 118°C)



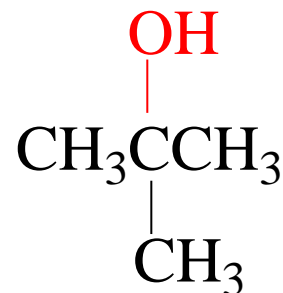
2-Methyl-1-propanol

(mol wt = 74; bp = 108°C)



2-Butanol

(mol wt = 74; bp = 99.5°C)



2-Methyl-2-propanol

(mol wt = 74; bp = 83°C)

- Boiling points of 1° alcohol > 2° alcohol > 3° alcohol



Note that

- boiling points increase with the increase of the number of hydroxyl groups .

Exercise:

1- Rank the following molecules in order of decreasing B.P.

Butanol

Pentanol

Propylchloride

Propanol

Butane

I

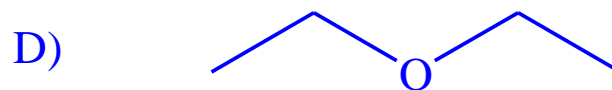
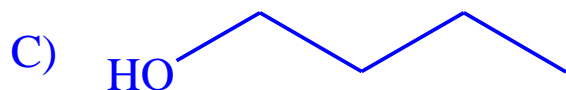
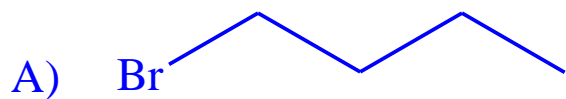
II

III

IV

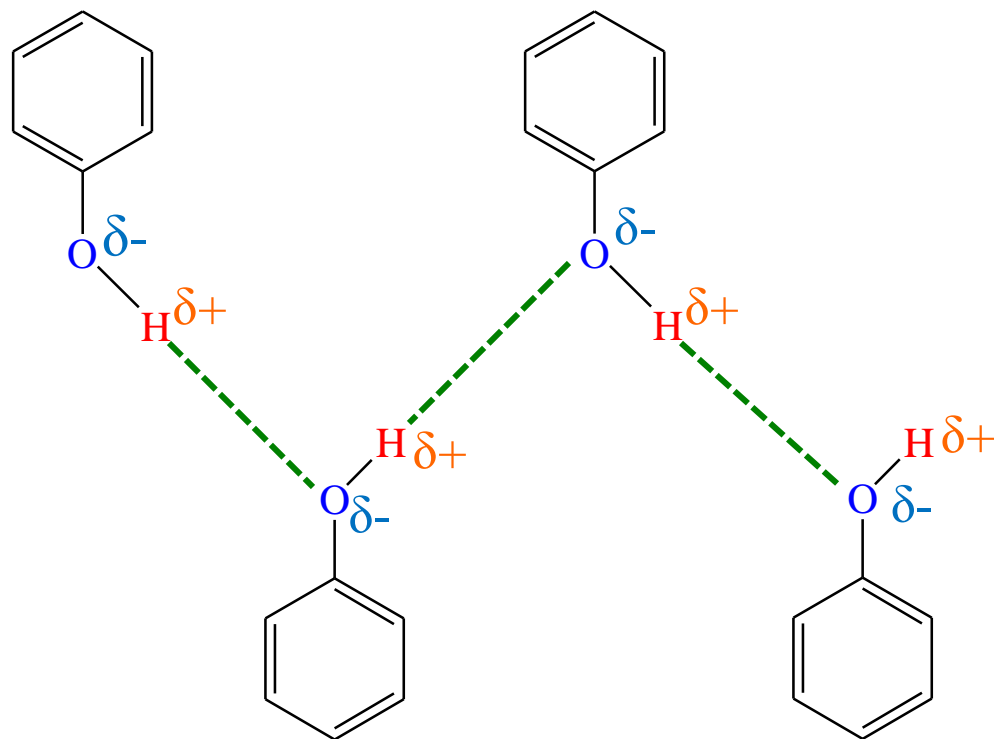
V

2- Which of the following molecules has the highest B.P?



- Phenols

Phenols tend to have **higher boiling points** than **alcohols** of similar molecular weight **because** they have **stronger intermolecular hydrogen bonding**.

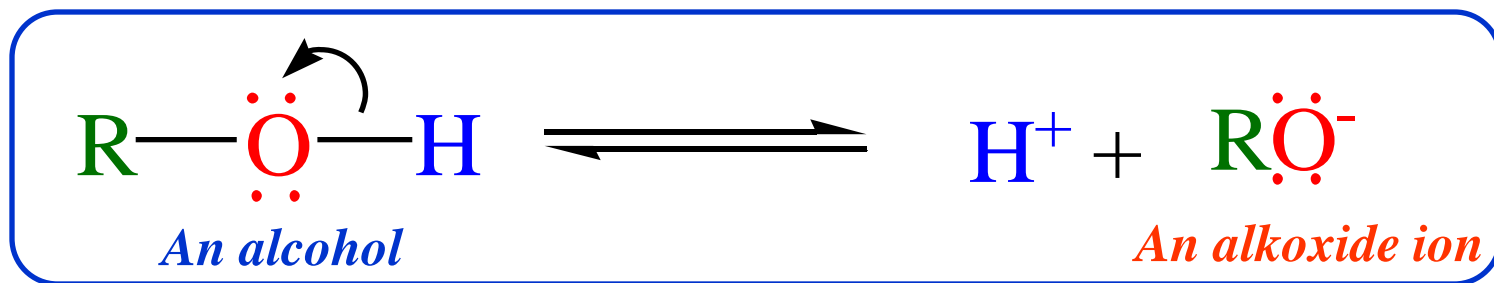


Representations of intermolecular hydrogen bonding in phenol

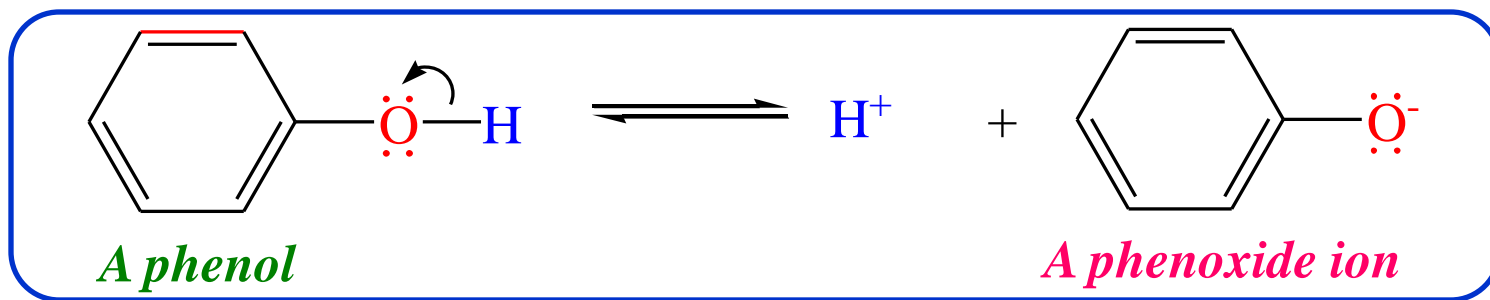
Acidity of Alcohols & Phenols

Both alcohol and phenol show acidic property to a certain degree since the hydrogen in the hydroxy group (-OH) can be removed by a base as a proton.

- Alcohols are *slightly acidic* (pKa 16-18).
- The anion derived by the deprotonation of an alcohol is the **alkoxide**.



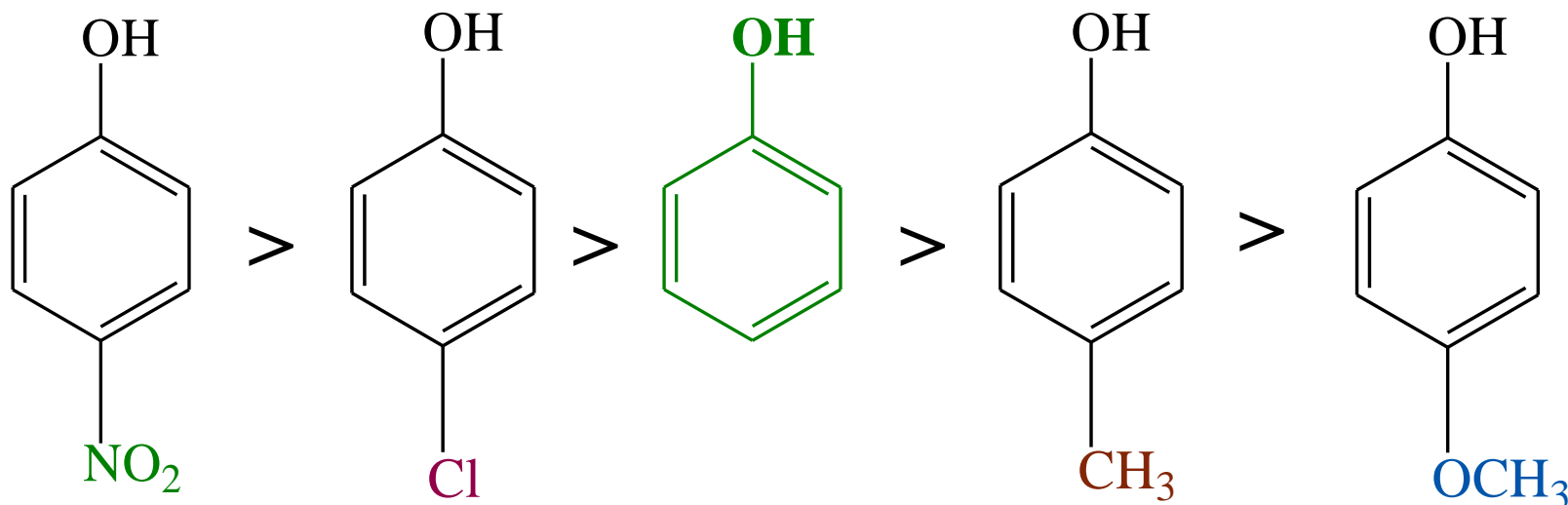
- Phenols are **more acidic** than alcohols.
- The pKa for most phenols is (10).
- The anion derived by the deprotonation of an phenols is the phenoxide ion.



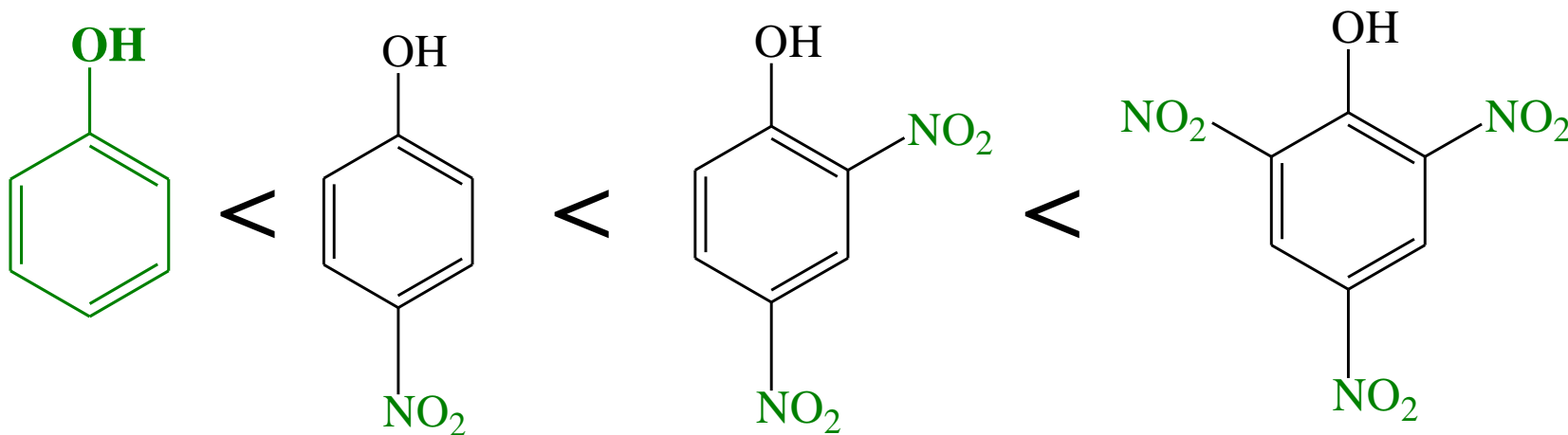
Effect of substituents on the acidity of phenols

- Introduction of **electron-withdrawing groups (EWG)**, such as NO_2 or CN , X on the ring increases the acidity of phenol.
- Also, introducing **electron-donating groups (EDG)**, such as NH_2 , R , OR decrease the acidity of phenols.

Acidity order



- The greater the number of electron withdrawing at *o*- and *p*-position, more in the acidic character of phenol.



Phenol

4-Nitrophenol

2,4-Dinitrophenol

2,4,6-Dinitrophenol

pK_a	10.0	7.2	4.0	0.4
--------	------	-----	-----	-----

pK_a values for substituted phenols.



Compound name	Ionization constant K _a	pK _a
Monosubstituted phenols		
Phenol	1.0×10^{-10}	10.0
<i>o</i> -Cresol	4.7×10^{-11}	10.3
<i>m</i> -Cresol	8.0×10^{-11}	10.1
<i>p</i> -Cresol	5.2×10^{-11}	10.3
<i>o</i> -Chlorophenol	2.7×10^{-9}	8.6
<i>m</i> -Chlorophenol	7.6×10^{-9}	9.1
<i>p</i> -Chlorophenol	3.9×10^{-9}	9.4
<i>o</i> -Methoxyphenol	1.0×10^{-10}	10.0
<i>m</i> -Methoxyphenol	2.2×10^{-10}	9.6
<i>p</i> -Methoxyphenol	6.3×10^{-11}	10.2
<i>o</i> -Nitrophenol	5.9×10^{-8}	7.2
<i>m</i> -Nitrophenol	4.4×10^{-9}	8.4
<i>p</i> -Nitrophenol	6.9×10^{-8}	7.2
Di- and trinitrophenols		
2,4-Dinitrophenol	1.1×10^{-4}	4.0
3,5-Dinitrophenol	2.0×10^{-7}	6.7
2,4,6-Trinitrophenol	4.2×10^{-1}	0.4

Example: In each of the following pairs of compounds, indicate which is more acidic.

(a) *p*-chlorophenol or *p*-nitrophenol

(b) 2,4-dinitrophenol or 3,5-dinitrophenol

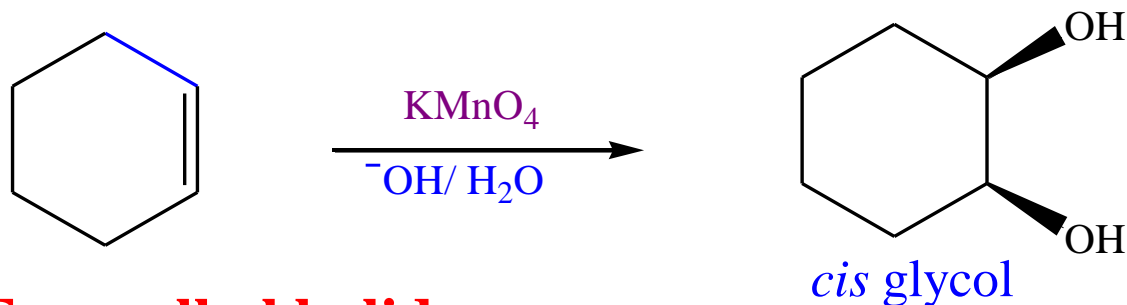
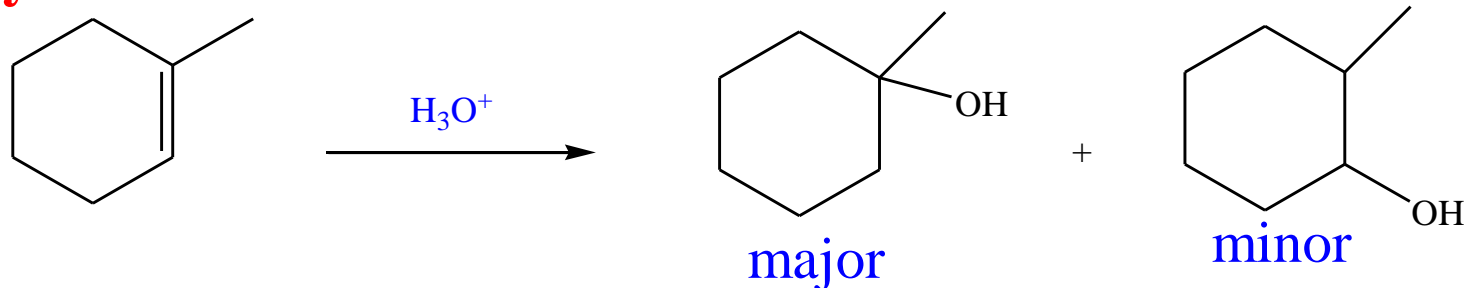
(c) *o*-Creasol or *o*-Nitrophenol

(d) *o*-Methoxyphenol or *m*-Methoxyphenol

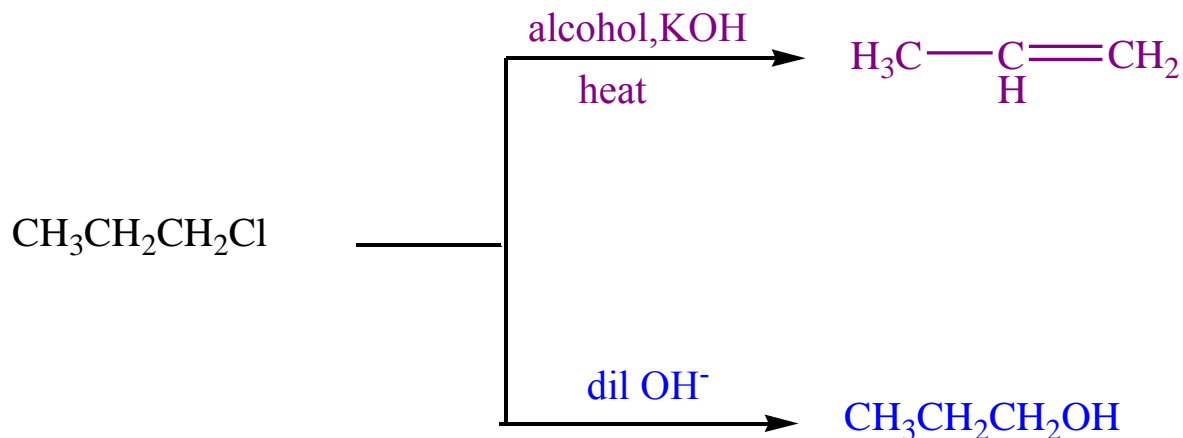
A. Preparation of alcohols:

Alcohols can be prepared by the following methods:

1- Hydration of alkenes

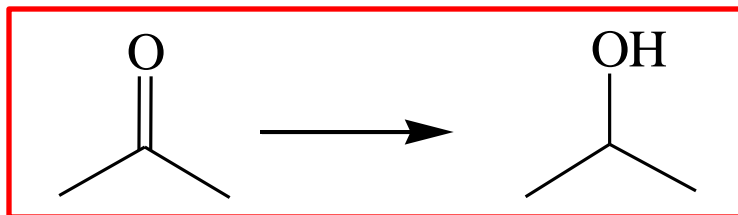


2- From alkyl halide

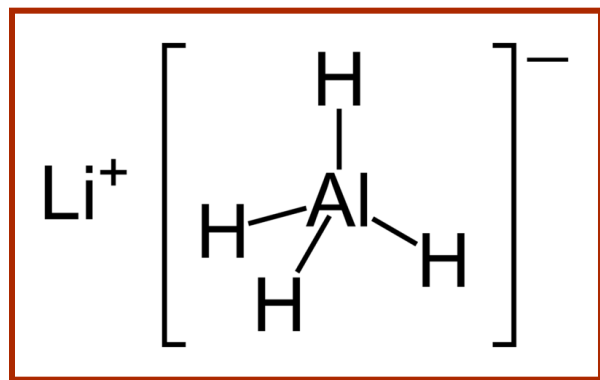


3-Reduction of Aldehydes, Ketones, Acids and Esters

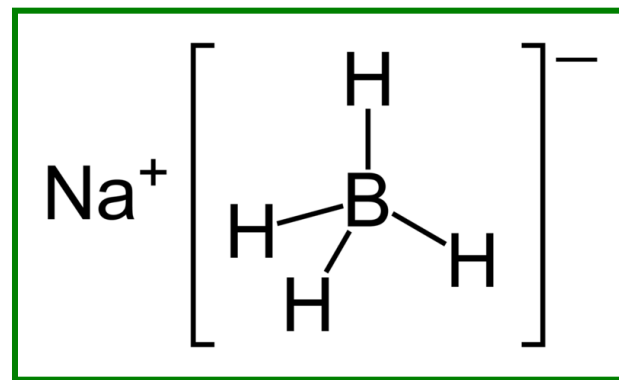
The **carbonyl group** of several functional groups may be converted to the **alcohol** by **reducing agents**.



Reducing Agents



Lithium aluminium hydride



**Sodium borohydride
or**

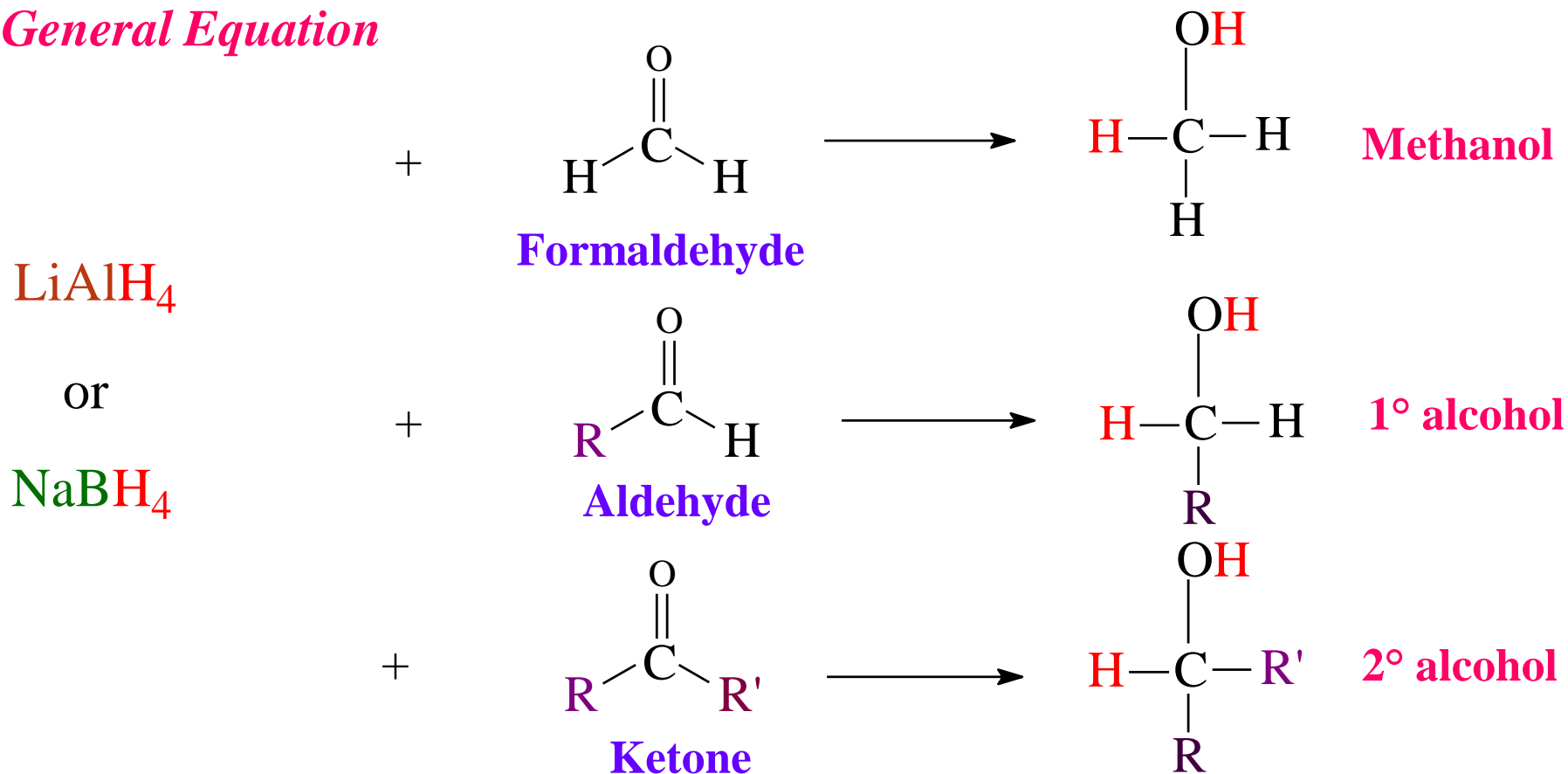
Sodium tetrahydridoborate

3-a. Reduction of Aldehydes and Ketones

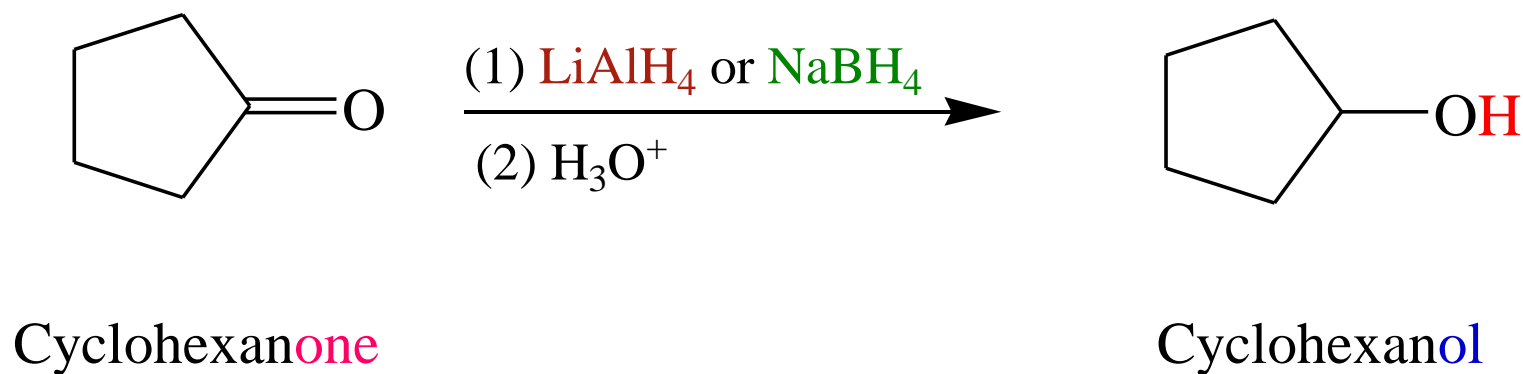
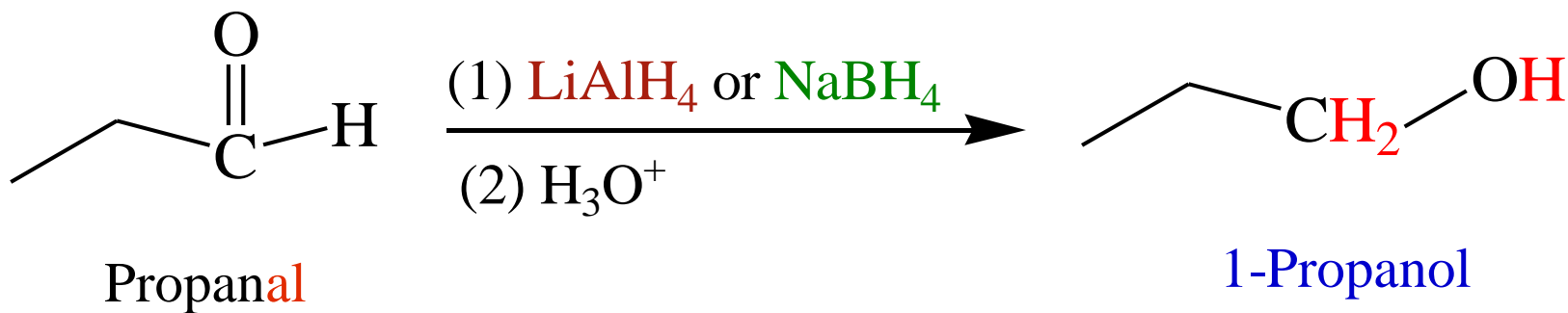
Aldehydes and ketones are most readily reduced with hydride reagents, LiAlH_4 or NaBH_4 .

The reducing agents LiAlH_4 and NaBH_4 act as a source of (hydride ion, H^-), the hydride reacts with the carbonyl group, $\text{C}=\text{O}$, in aldehydes or ketones to give alcohols.

General Equation



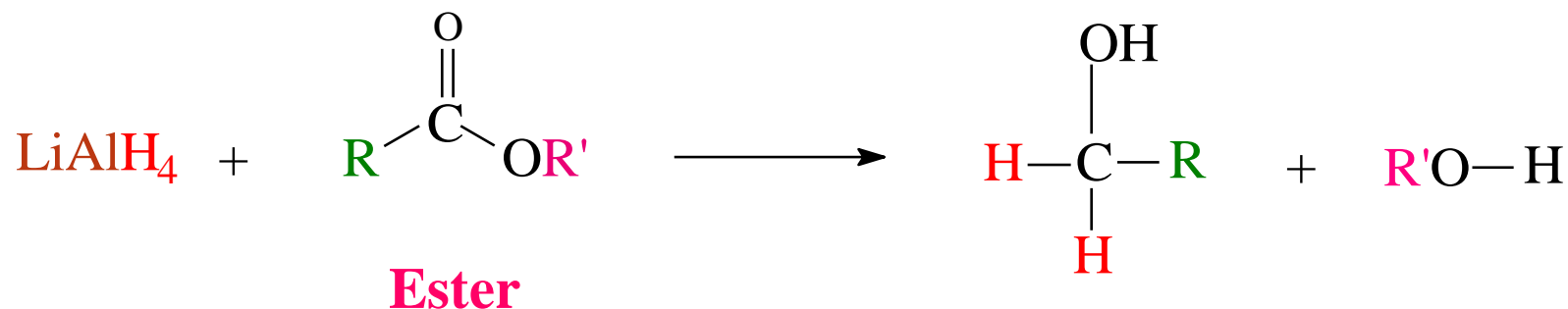
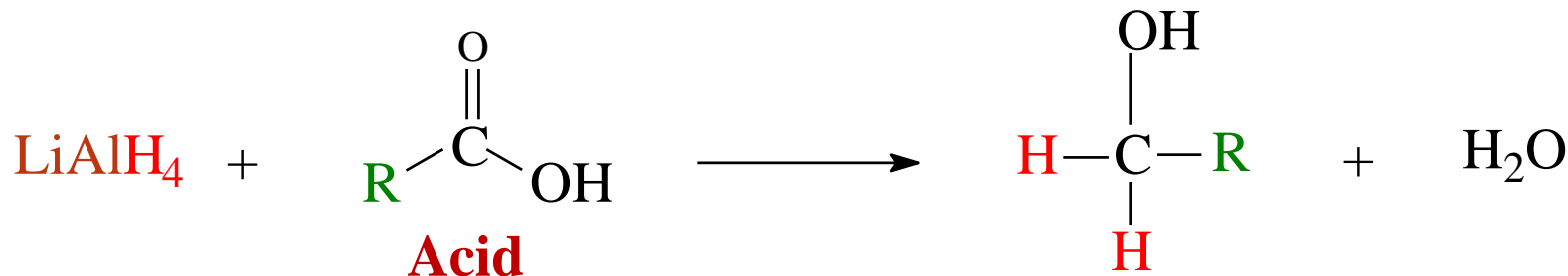
Examples



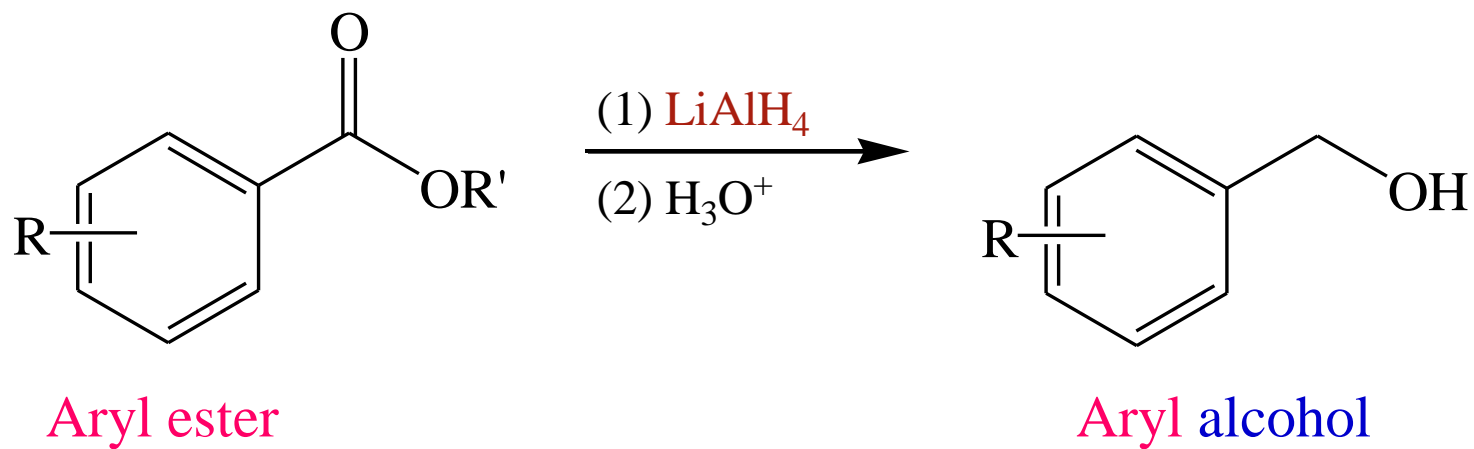
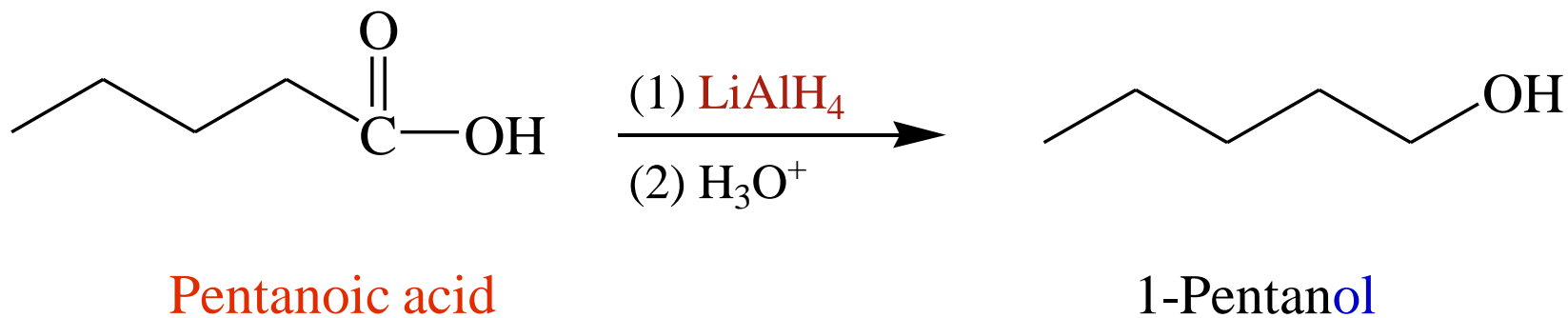
3-b. Reduction of Acids and Esters

- Carboxylic acids and esters are less reactive to Nu than aldehydes or ketones.
- As a result they can only be reduced by LiAlH_4 but NOT by the less reactive NaBH_4 .
- Each reaction requires that 2 hydrides (H^-) be added to the carbonyl of acids or esters.

General Equation



Examples



4- From Grignard reagent

- ❑ The special value of *Grignard reagents* is that they provide excellent ways to form new C-C bonds.
- ❑ As a result of the difference in electronegativity between carbon and magnesium the charge distribution in the *Grignard reagent* is such that the organic group (R) is *partially negative* and the -MgX group is *partially positive* [$\text{R}^{\delta-}\text{Mg}^{\delta+}\text{X}$].
- ❑ Grignards react with aldehydes and ketones to give intermediate products that form alcohols when hydrolyzed.

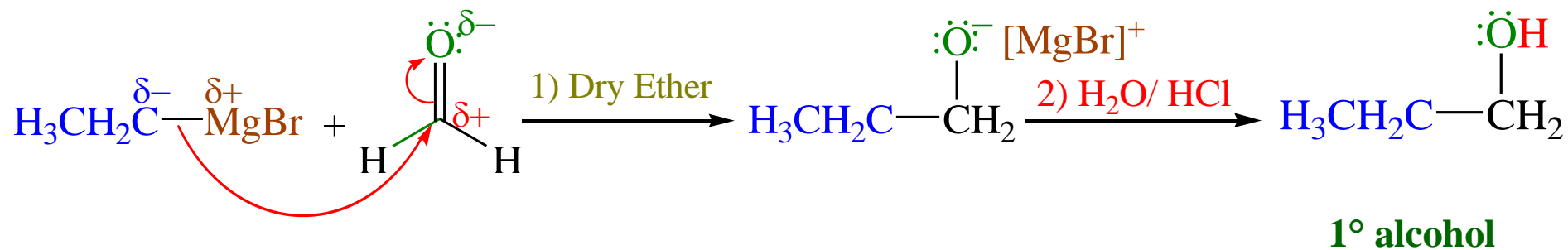
Grignard reagent + formaldehyde \rightarrow 1° ROH

Grignard reagent + other aldehydes \rightarrow 2° ROH

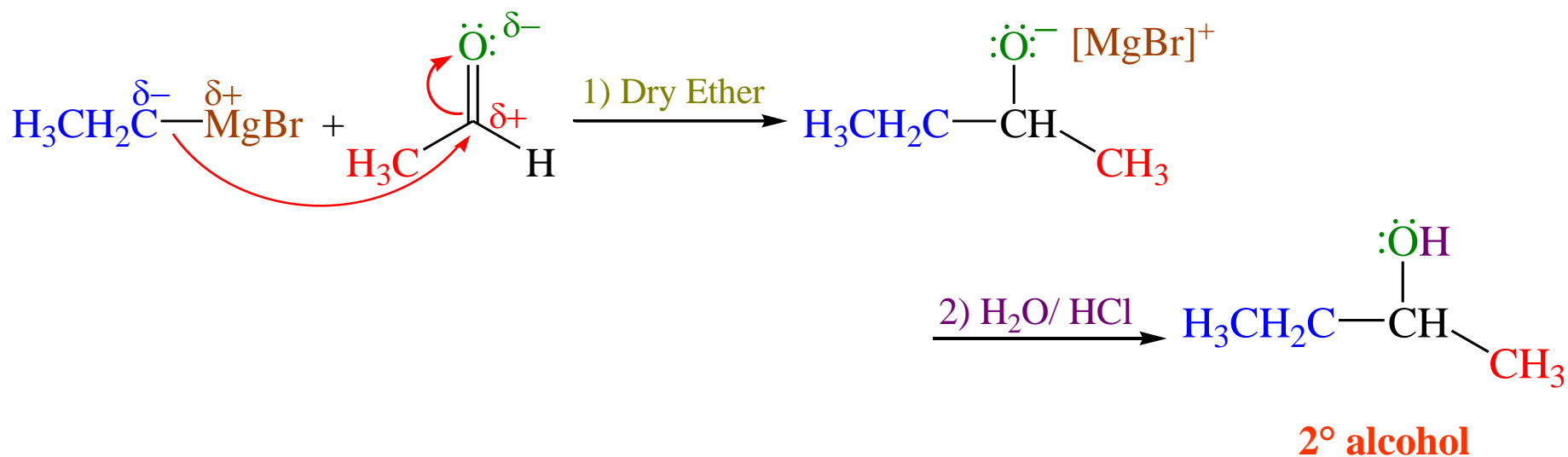
Grignard reagent + ketones \rightarrow 3° ROH

Grignard reagent + Esters \rightarrow 3° ROH

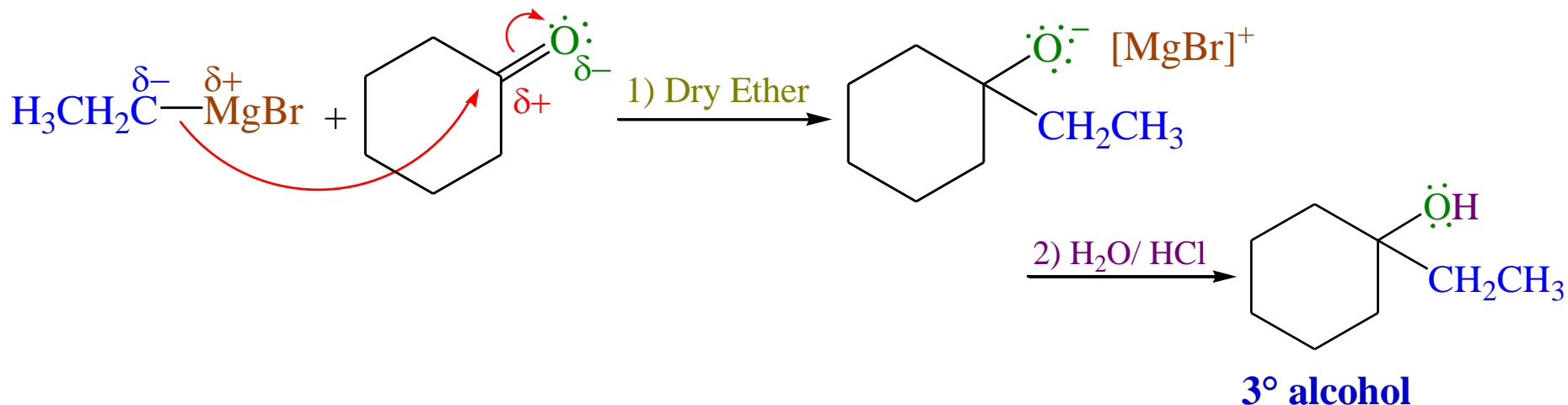
4.1-Grignard + **formaldehyde** yields a **primary alcohol** with one additional carbon.



4.2-Grignard + **aldehyde** yields a **secondary alcohol**.

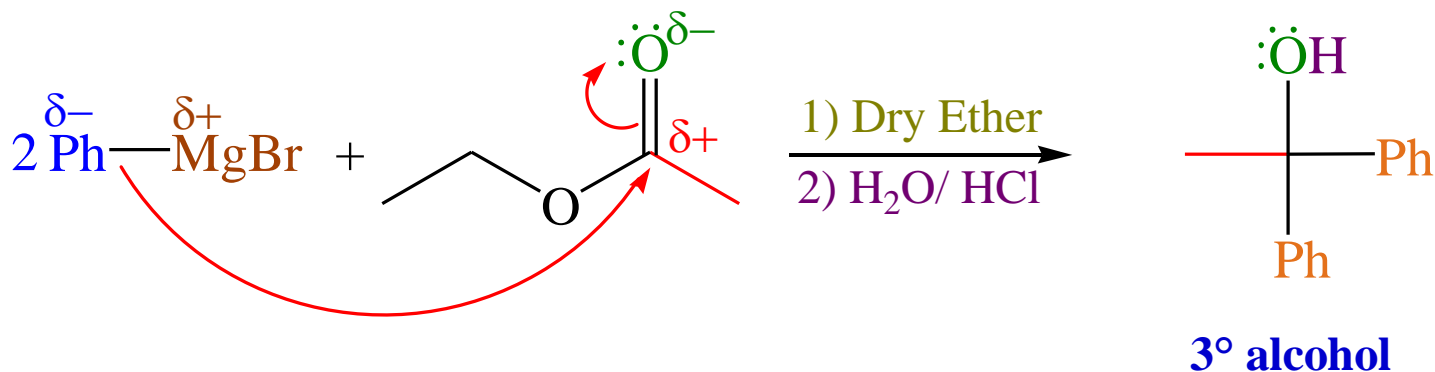


4.3-Grignard + ketone yields a tertiary alcohol.



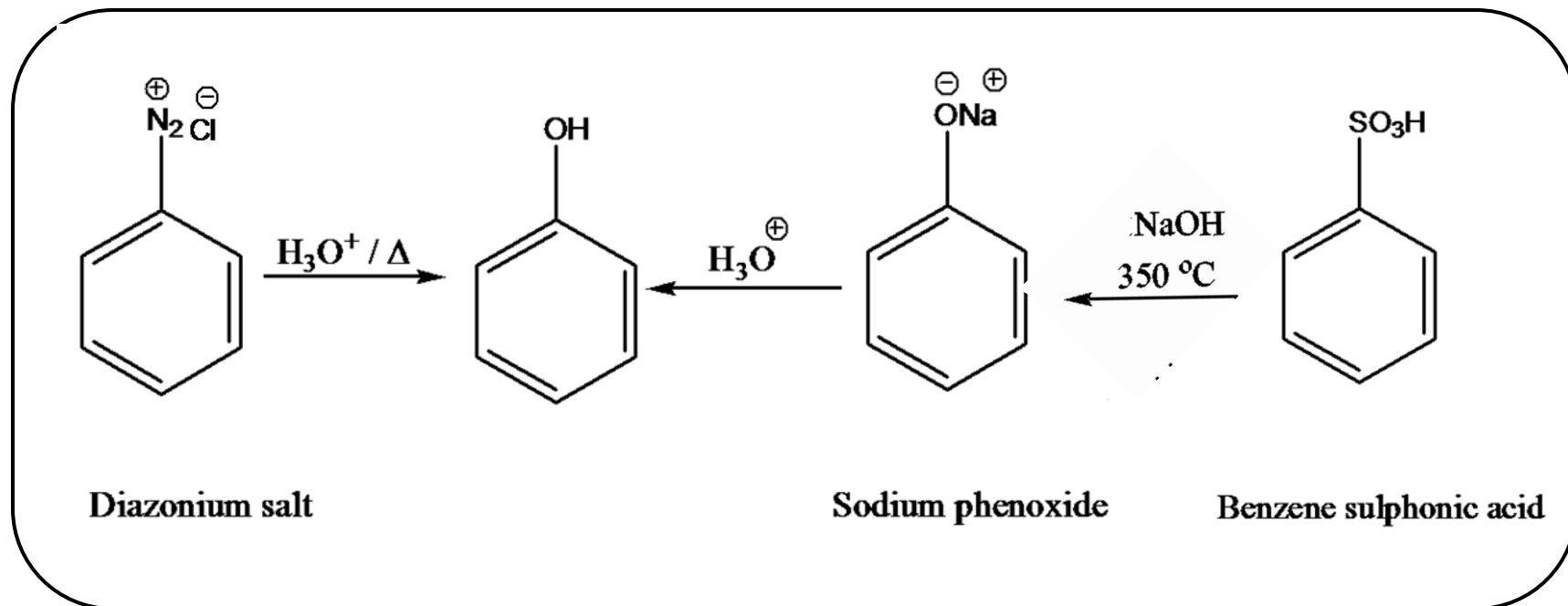
4.4 -Grignard + ester yields a tertiary alcohol.

The **esters** are less reactive than **aldehydes** and **ketones**. However they give **tertiary alcohols** with excess (**2 moles**) of **Grignard reagent**.



Preparation of phenols

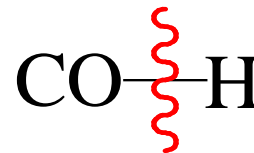
□ Hydrolysis of diazonium salt.



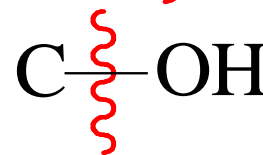
Reactions of alcohols and phenols

I-Reactions of alcohols: Alcohols undergo **two kinds** of reactions;

1-Those that involve the breaking of **oxygen-hydrogen** bond



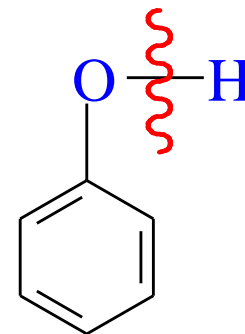
2- Those that involve the rupture of **carbon-oxygen** bond



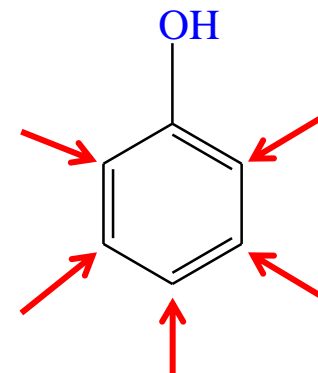
II-Reactions of phenols:

phenols undergo **two kinds** of reactions;

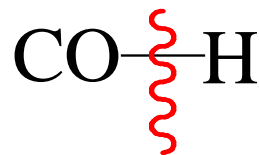
1-Those that involve the breaking of **oxygen-hydrogen** bond



2-Those that involve the **benzene ring** reactions.



A- Reactions involving oxygen-hydrogen bond breaking

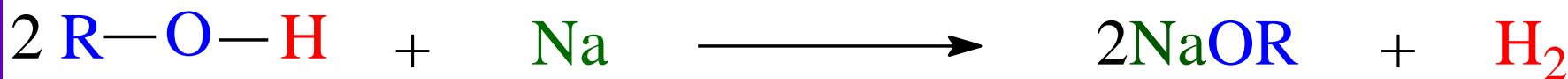


(1) Salt Formation

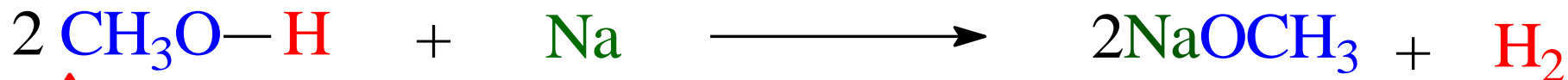
Alcohols and phenols can act as acids whenever they donate a proton to a base.

Alcohols with alkali metals (*active metals*) like sodium Na or Potassium K to form the salt (alkoxide).

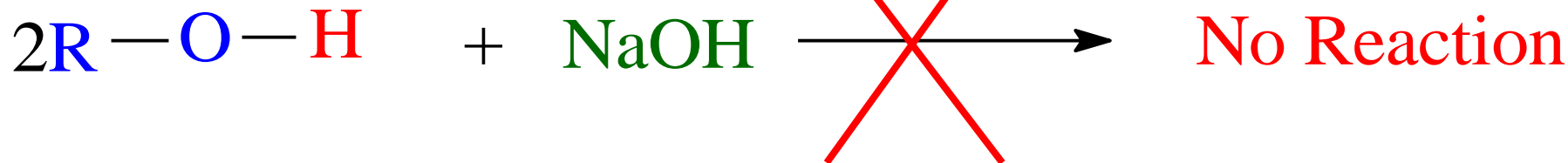
General Equation



Example

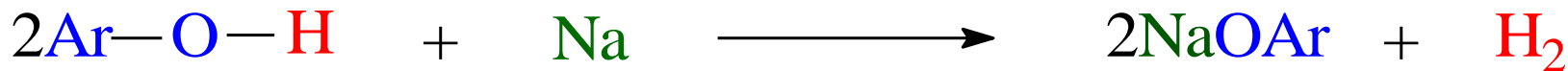


Note That

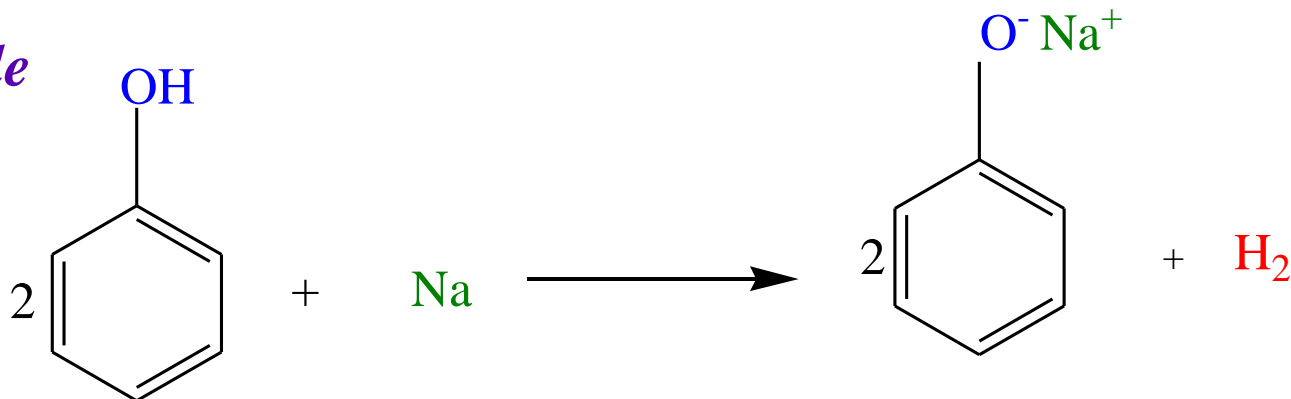


✓ Phenols are **more acidic** than **alcohols** and may be converted to their sodium salts by reaction with aqueous **NaOH**; **sodium hydroxide**.

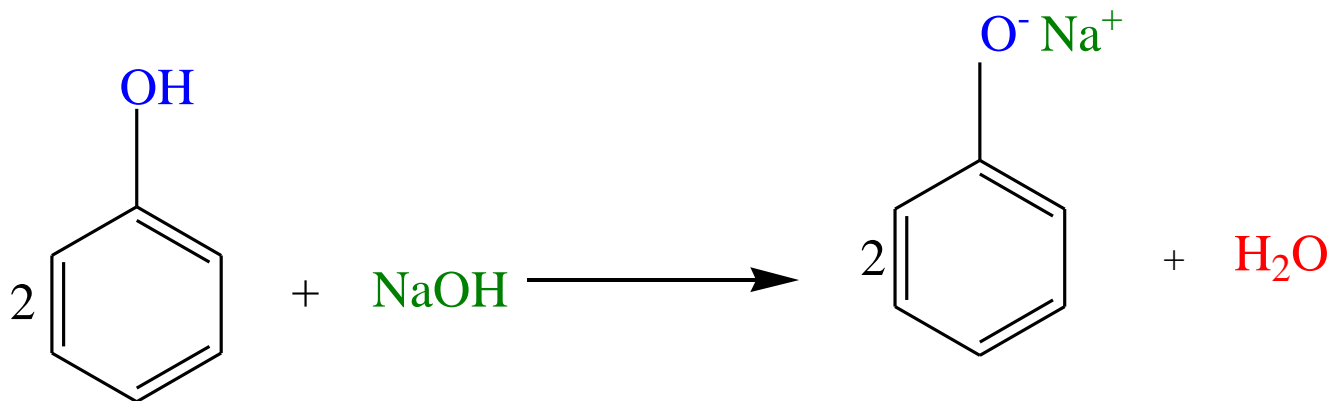
General Equation



Example



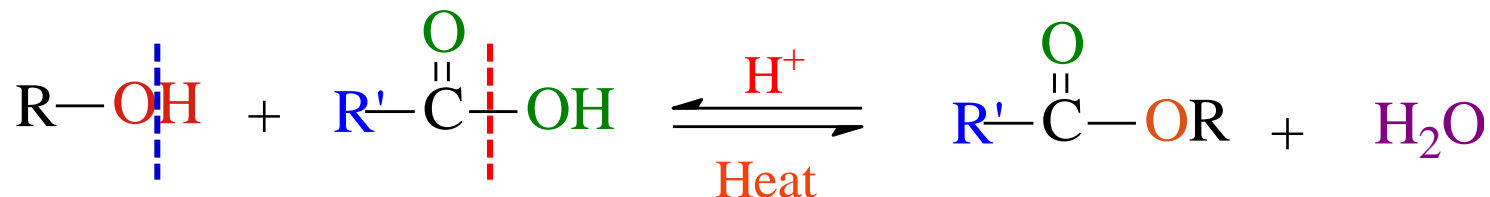
Note That



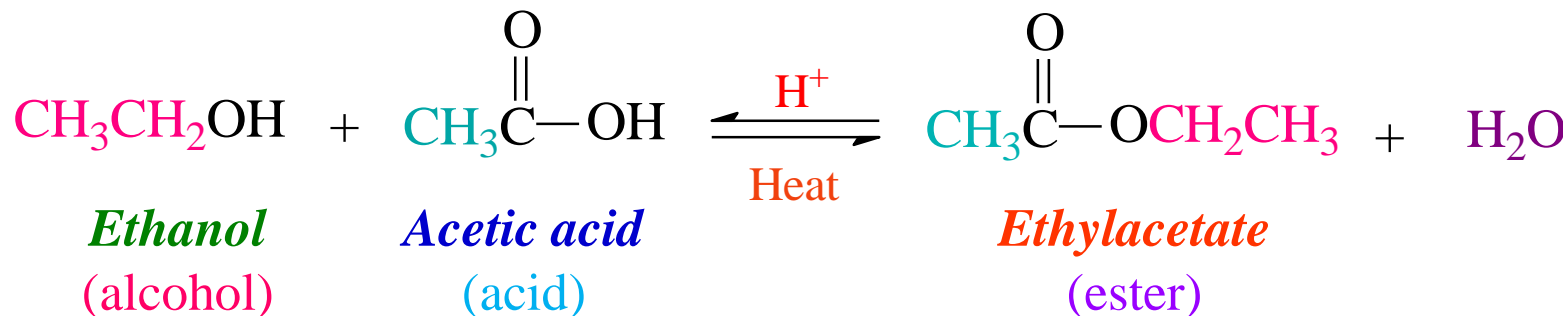
(2) Reaction of alcohols with carboxylic acids :*Ester formation*

Alcohols can be converted to esters by means of the *Fischer Esterification Process*. In this method, an alcohol is reacted with a carboxylic acid in the presence of an inorganic acid catalyst such as, H_2SO_4 or HCl .

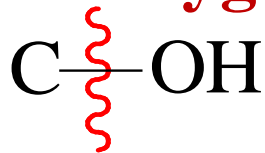
General Equation



Example



B- Reactions involving carbon-oxygen bond rupturing



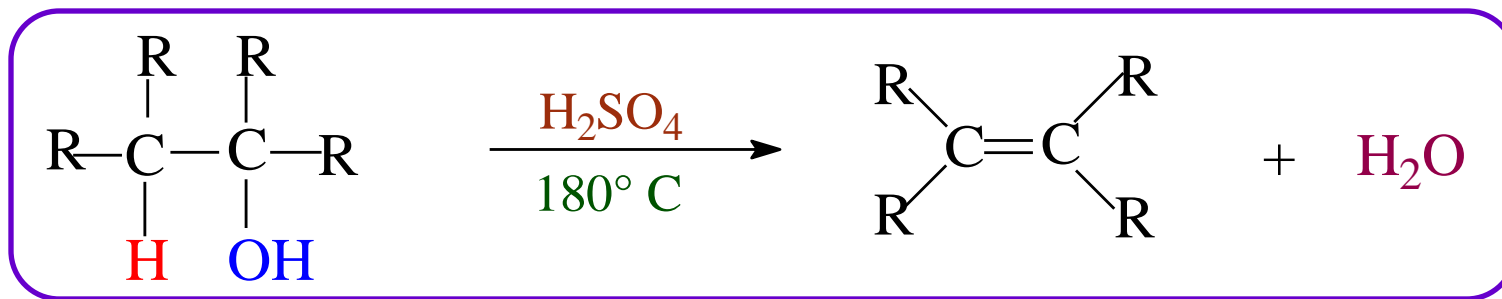
1- Dehydrations of alcohols:

1.1 Formation of alkenes.

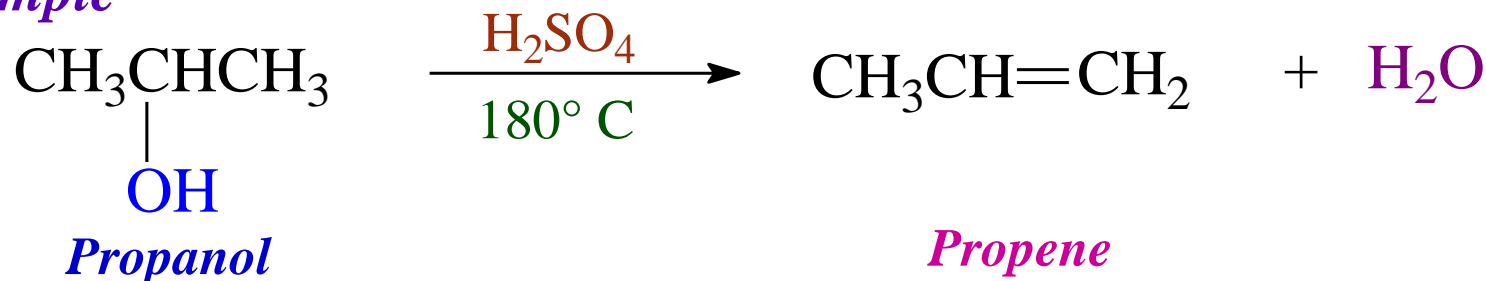
- Heating **alcohols** in concentrated sulfuric acid (H_2SO_4) at **180°C** removes the **OH group** and a **H** from an **adjacent carbon** to produce an **alkene**, with **water** as a by-product.

Since **water** is “**removed**” from the **alcohol**, this reaction is known as a **dehydration reaction** (or an **elimination reaction**):

General Equation

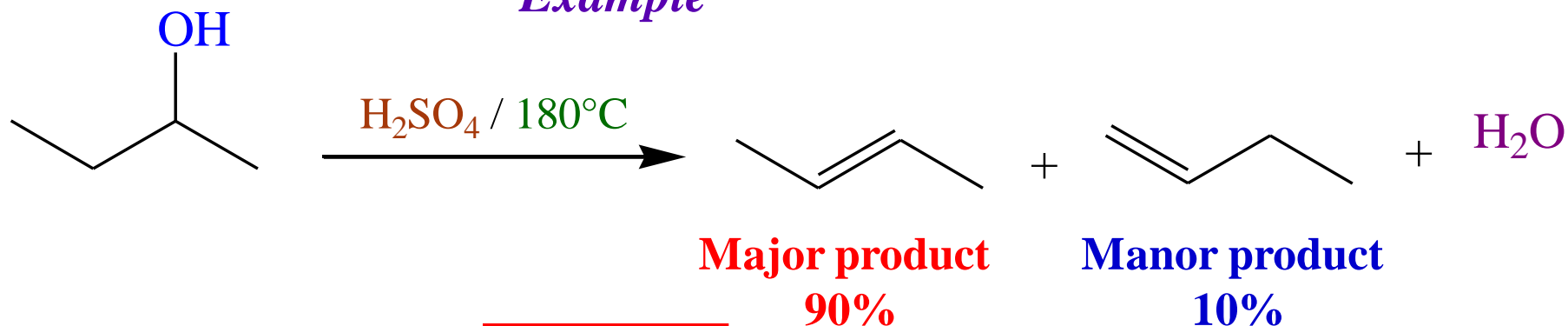


Example

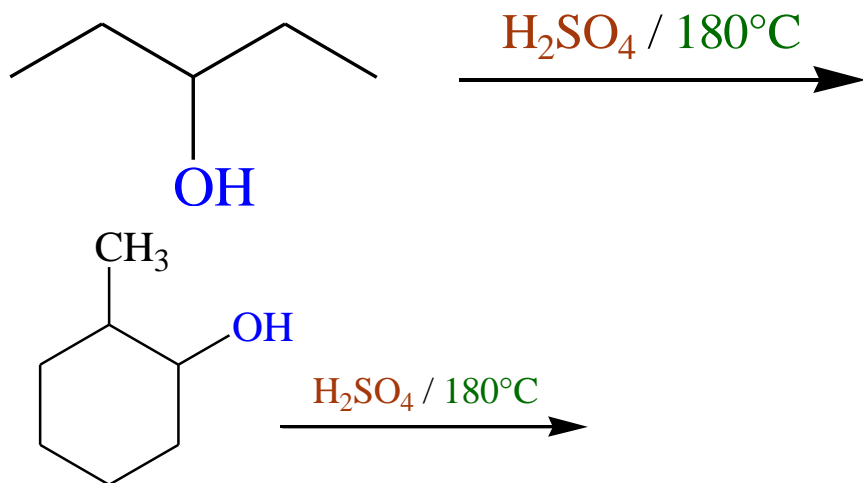


- If there is more than one possible product of a **dehydration reaction**, the major product can be predicted from **Zaitsev's Rule**:
- **Zaitsev's Rule**— when an alkene is produced in an **elimination reaction**, the major product is the one with **the more highly substituted double bond**.

Example



Exercise

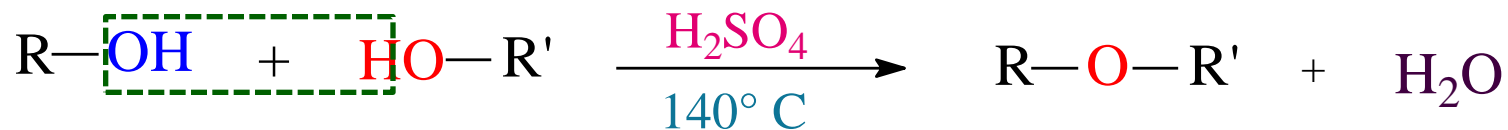


1-Dehydration of Alcohols :

1.2 Ethers Formation

- Heating alcohols (R—OH) in concentrated sulfuric acid (H_2SO_4) at 140°C removes a molecule of water from two alcohol molecules, causing the two “R” groups to become attached to an oxygen atom, forming an ether functional group:

General Equation



Examples



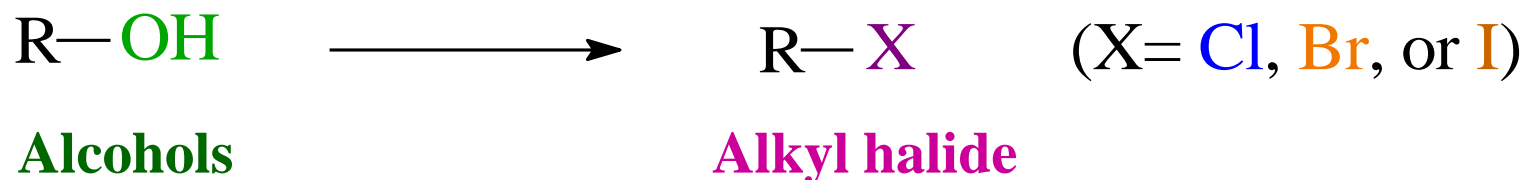
Ethanol

Diethylether

2- Replacement of the OH group by Halide: *Alkyl Halides Formation*.

The hydroxyl group -OH of alcohols can be replaced by halide to form alkyl halides.

The net equation is:



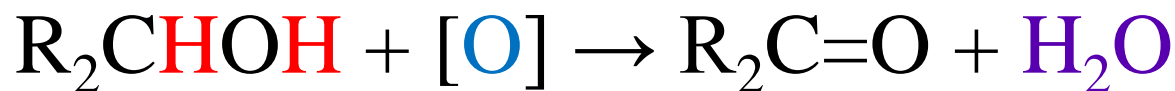
Alkyl fluoride; R—F, are not prepared from alcohols.

Replacement of the OH group by Halide

- *1-Reaction with hydrogen halides HX: Lucas test.*
- *2-Reaction with thionyl chloride SOCl₂.*
- *3-Reaction with phosphorus halides, PX₃ or PX₅.*

Oxidation of Alcohols to Carbonyl Compounds

- An oxidation reaction occurs when a molecule **loses electrons**. This is usually manifested as **an increase in the number of oxygen atoms** or a **decrease in the number of hydrogen atoms**.
- Some **common oxidizing agents** include potassium permanganate (KMnO_4), chromic acid (H_2CrO_4), sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$), and other Cr^{6+} salts.
- **Alcohols** can be oxidized by removing **two H** atoms from the molecule; the exact products of the reaction will depend on the type of alcohol.



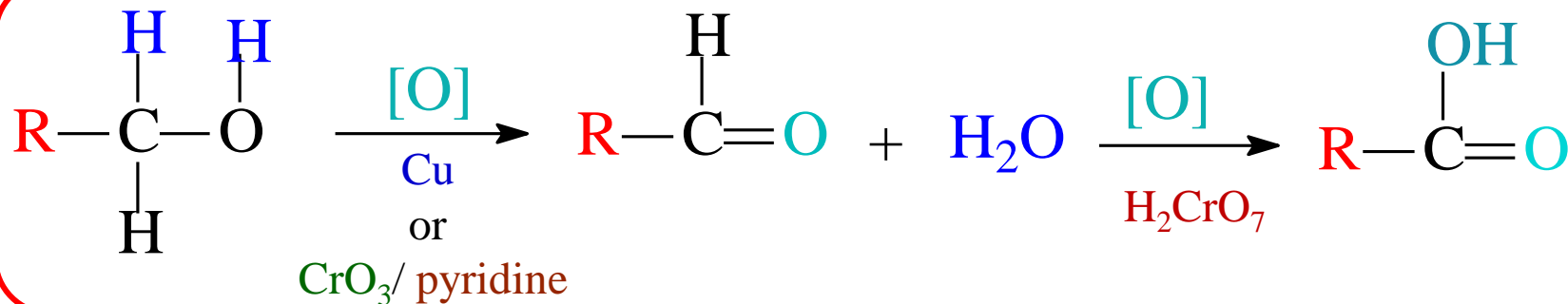
$[\text{O}] = \text{oxidation}$

- Oxidation of alcohols gives different products depending on; the class of alcohols that is oxidized & the kind of oxidizing agent that is used.

A- Oxidation of Primary alcohols

- Primary alcohols yields aldehydes when treated with mild oxidizing agent such as hot metallic copper; Cu or CrO₃ in pyridine .
- When 1° alcohols are allowed to react with stronger oxidizing agents, such as chromic acid, H₂CrO₇, or neutral potassium permanganate, KMnO₄, the intermediate aldehydes formed initially are oxidized further to carboxylic acids, RCOOH.

General Equation



1° alcohol

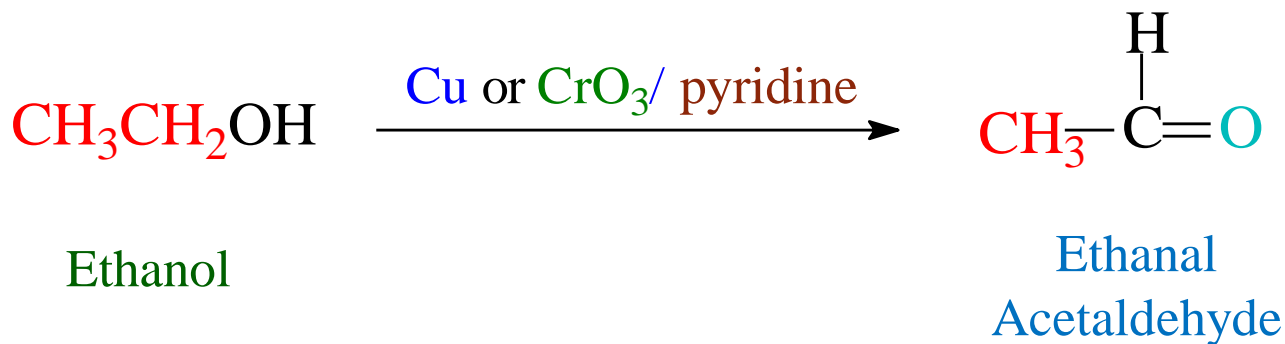
Aldehyde

Carboxylic acid

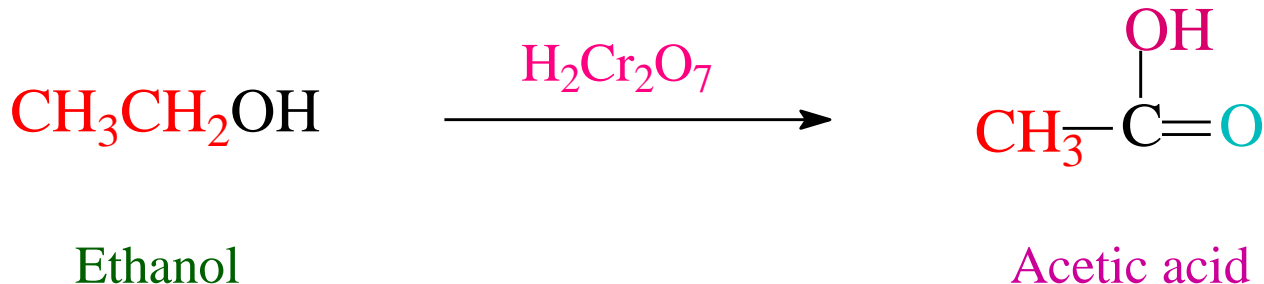
✓ oxidation of **primary alcohols** to **aldehydes** requires special reagents to avoid over-oxidation to the **acid**.

Example

with mild oxidizing agent



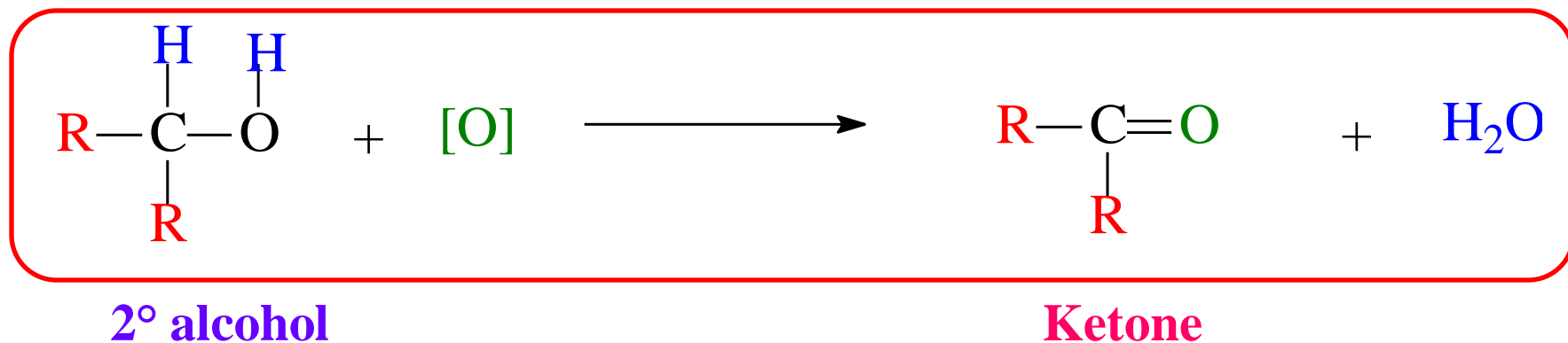
with stronger oxidizing agents



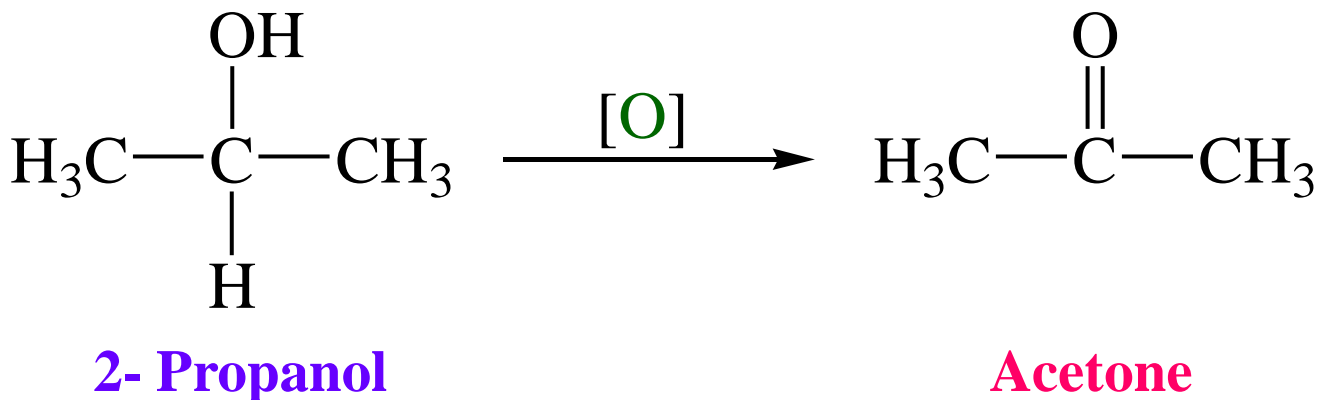
B- Oxidation of 2° Secondary Alcohols

Secondary alcohols are oxidized to **ketones**, which cannot be oxidized any further:

General Equation

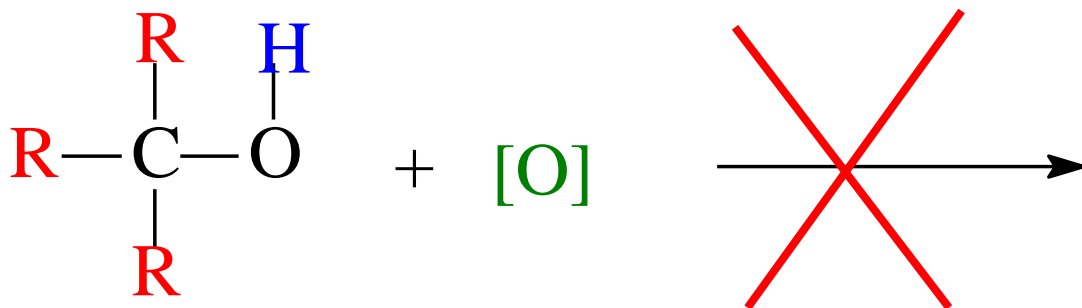


Example



C- Oxidation of 3° Tertiary Alcohols

Do not react with oxidizing agents under normal conditions.



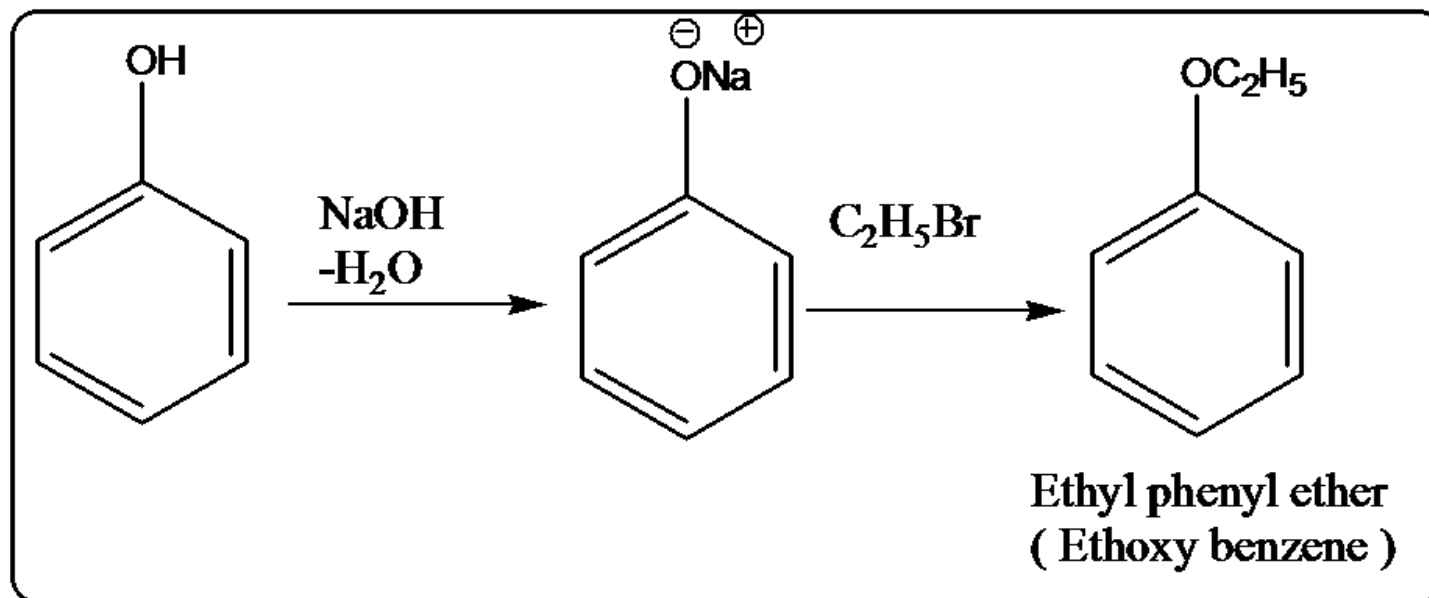
3° Tertiary alcohol



Note That

- ✓ Tertiary are **stable** to oxidation under **normal conditions**.
- ✓ under **drastic conditions**, tertiary alcohols give **ketones** and **acids**, each containing less carbons than **alcohols**.

Reactions of phenols

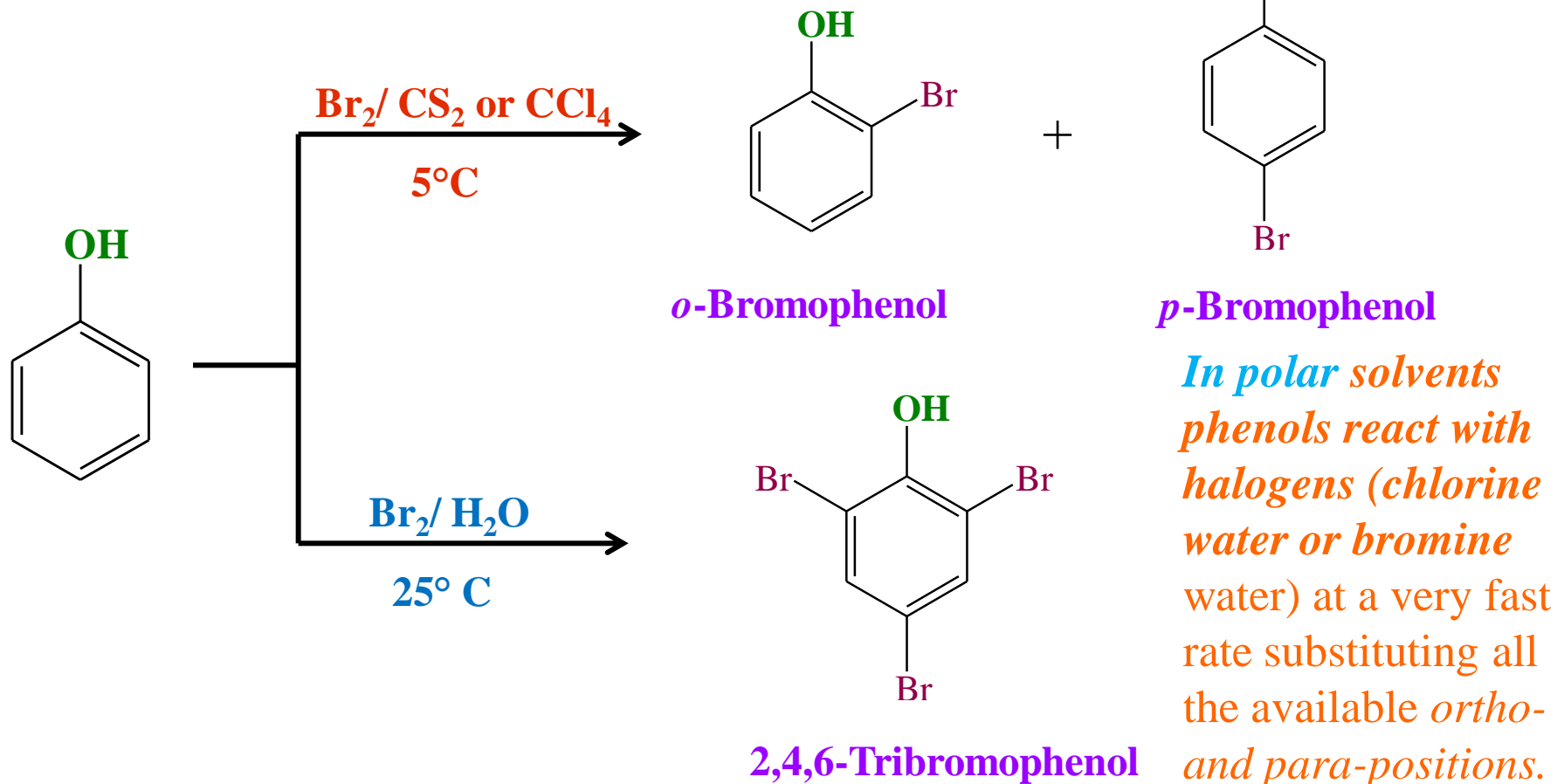


6- Reaction of aromatic ring of phenols

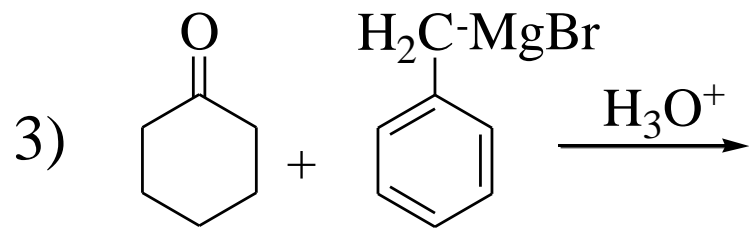
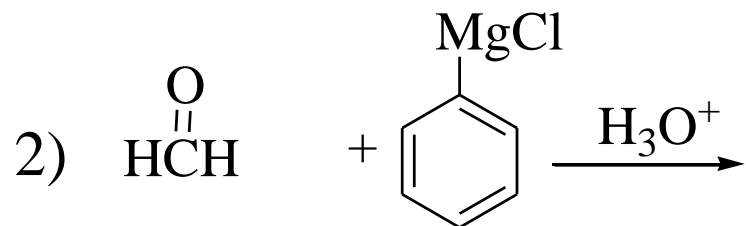
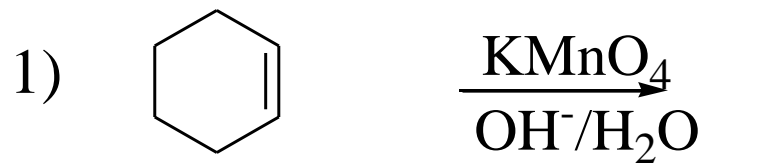
1-Halogenation

Electrophilic Substitution Reaction

However, halogenation can be stopped at *monohalogenation stage* if reaction is carried out in presence of *non-polar* or *less polar* solvents at low temperature.



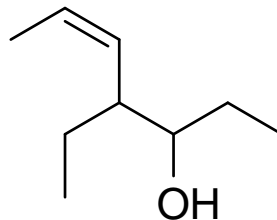
Home Work



4) The IUPAC name of

is:

- A) 4-Ethyl-5-heptyn-3-ol
- B) 4-Ethyl-5-heptan-3-ol
- C) 4-Ethyl-5-hepten-3-ol
- D) 4-Etyl-2-hepten-5-ol



5) The IUPAC name of

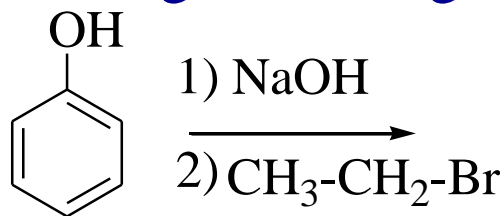
is:

- A) 3-Methyl-1-bromocyclohexanol
- B) 2-Bromo-3-methylcyclohexanol
- C) 4-Bromo-2-methylcyclohexanol
- D) 3-Bromo-1-methylcyclohexanol

6) The common name of 2-methyl-2-propanol is:

- A) Allyl alcohol
- B) Isopropyl alcohol
- C) *tert*-Butyl alcohol
- D) Benzyl alcohol

7) The following reaction gives



- A) 4-Ethylphenol
- B) 2-Ethylphenol
- C) Ethylphenyl ether
- D) Ethylphenyl ketone

*Thank you
For your attention*

