Alcohols and Phenols

Chapter 7

1432-2011

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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 Alkenes

  2- Hydroboration-Oxidation “ **anti-Markovnikov**”

  B. Preparation of Phenols

Reactions of Alcohols and Phenols:

I. Alcohols and Phenols as acids: Salt Formation

II. Oxidation

A. Oxidation of Alcohols

B. Oxidation of Phenols

III. Reactions Involving Carbon-Hydroxyl Bond Breaking

A. Formation of ester

B. Replacement of the OH Group by Halide: Alkyl Halides

1- Reaction with Hydrogen halides HX

2- Reaction thionylhalide SOX_2

3- Reaction with phosphorus trihalide PX_3 or PX_5

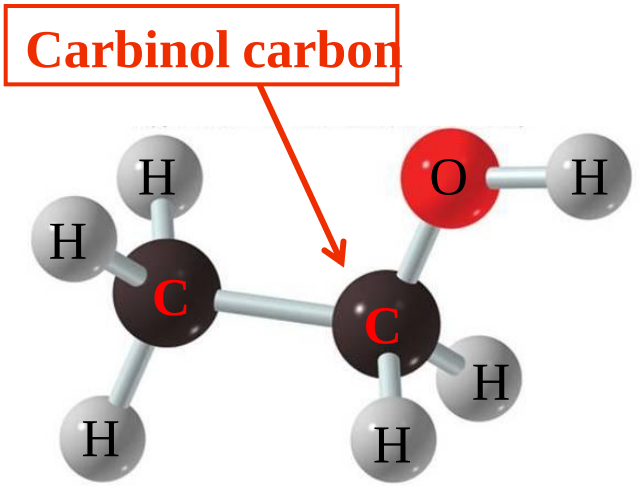
C. Dehydration of Alcohols: Formation of Alkenes

Introduction

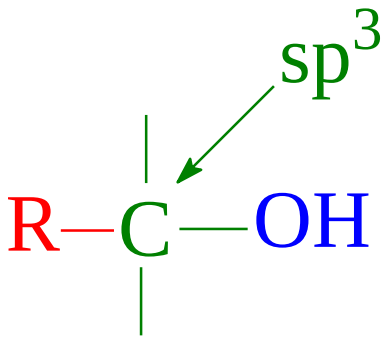
Alcohols

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

-The general formula for Alcohols is R—OH



The C-OH group is called ***the carbinol group***, and the carbon of this group is called "carbinol carbon".

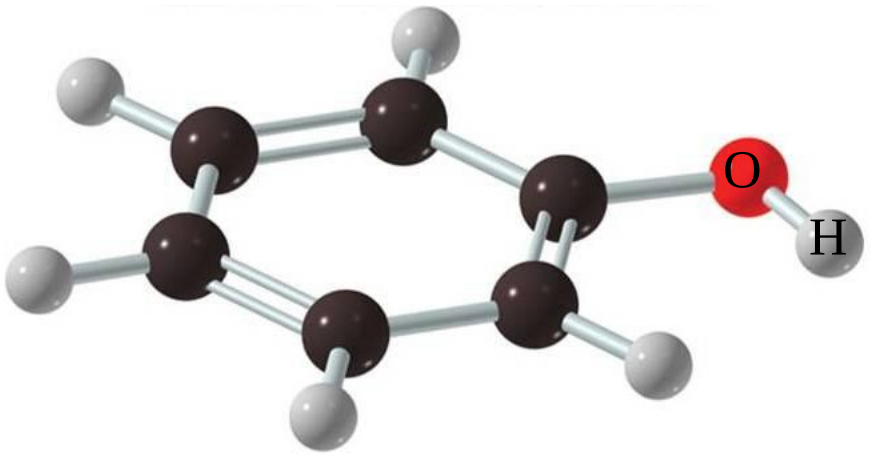


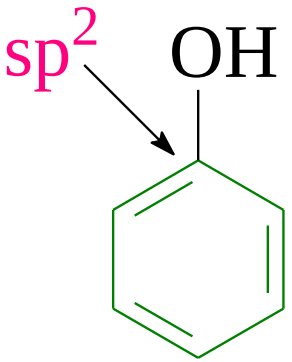
As all alcohols are the compounds containing hydroxyl group (-OH) attached to the alkyl group, so the carbinol carbon hybridization is sp3

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.



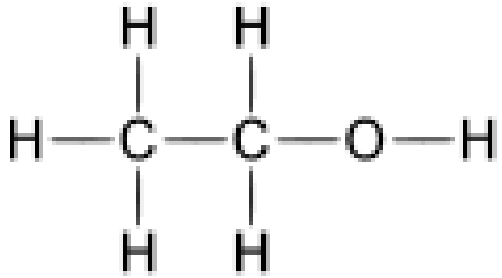


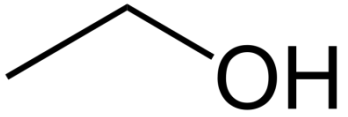
Phenols , ArOH

Types Of Alcohols

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

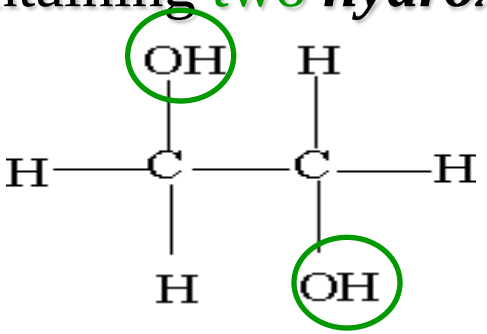
Example; ethanol (C_2H_5OH)

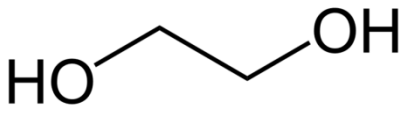




2. Dihydroxyls (glycols): containing two ***hydroxyl groups*** connected by <u>different</u> carbon atoms

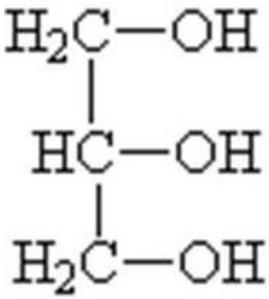
Example; Ethylene glycol (CH_2OH-CH_2OH).

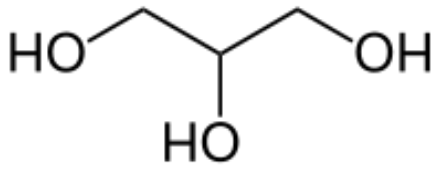




3. Polyhydroxyls: containing more than two ***hydroxyl groups*** on <u>different</u> carbon atoms

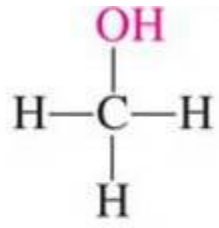
Example; 1,2,3-propanetriol (CH_2OH-$CHOH$-CH_2OH).



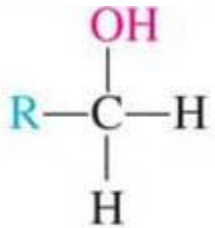


Classification of Monohydroxyl Alcohols

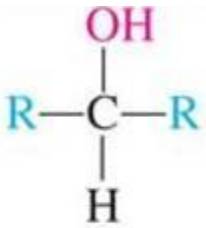
➢ ***The mono hydroxyl alcohols*** can be classified **into three types** according to the type of the carbon atom connected to the hydroxyl group:



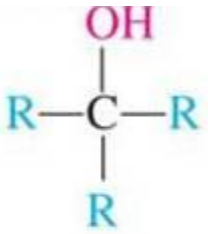
Methyl alcohol



1° Alcohol



2° Alcohol

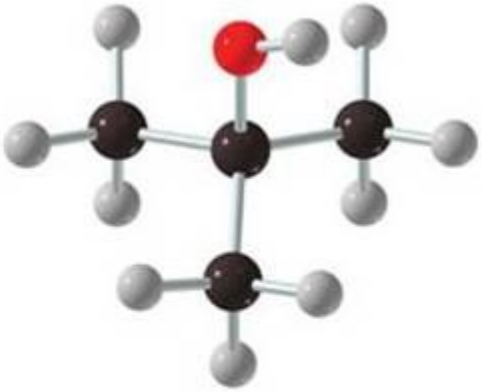


3° Alcohol

Methanol
(methyl alcohol)

Ethanol
(1° alcohol)

2-Propanol
(2° alcohol)



2-Methyl-2-propanol
(3° alcohol)

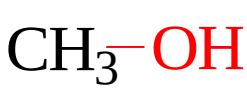
Nomenclature

1) Common Nomenclature (Alkyl + alcohol)

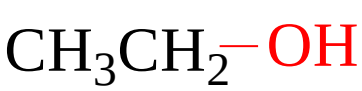
- You can use both the common and IUPAC systems to name alcohols.

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

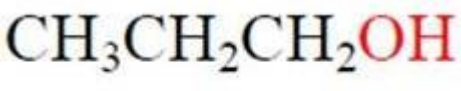
-Some examples of alcohols and their common names:



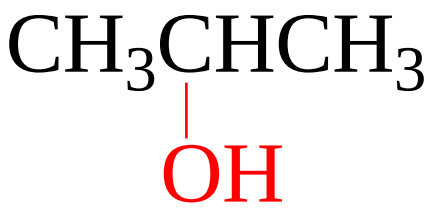
Methyl alcohol



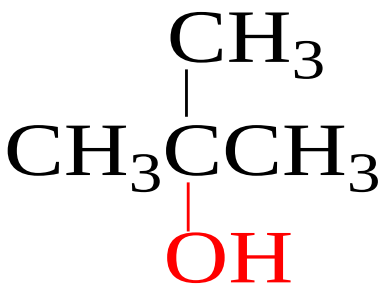
Ethyl alcohol



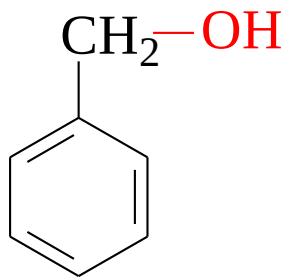
propyl alcohol



Isopropyl alcohol



t-butyl alcohol



Benzyl alcohol

Vinyl alcohol

Allyl alcohol

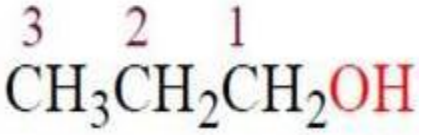
2) IUPAC Nomenclature

1) Select the **longest continuous carbon** **chain** ***to which the hydroxyl is directly attached.***

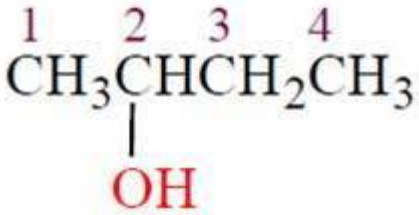
2) Change the name of the **alkane** **corresponding to this chain by dropping the final -e and adding the** ***suffix –ol***

3) **Number the longest continuous carbon chain so as to give the carbon atom** bearing the hydroxyl group **the lower number.**

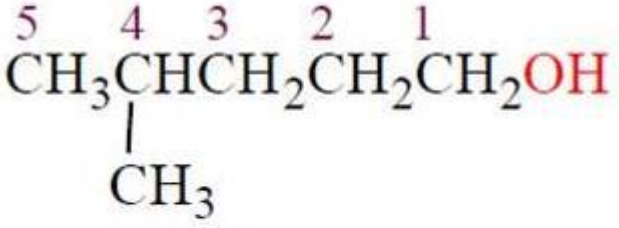
Examples



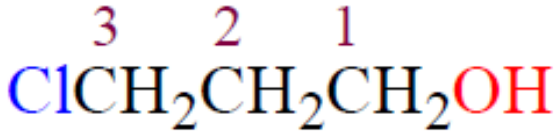
1-Propanol



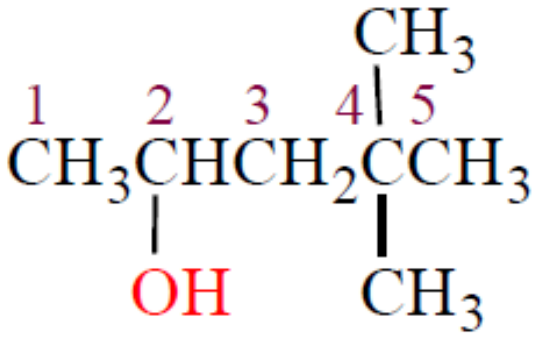
2-Butanol



4-Methyl-1-pentanol
(not 2-methyl-5-pentanol)

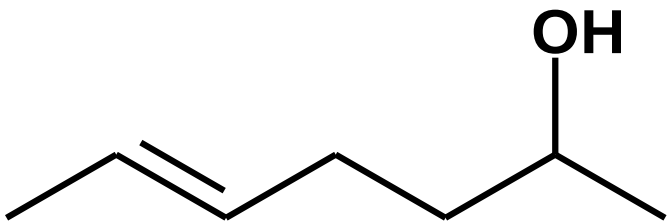


3-Chloro-1-propanol



4,4-Dimethyl-2-pentanol

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

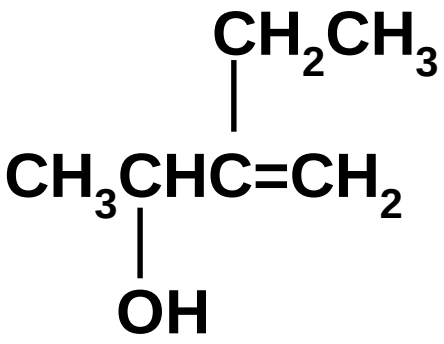


5-Hepten-2-ol

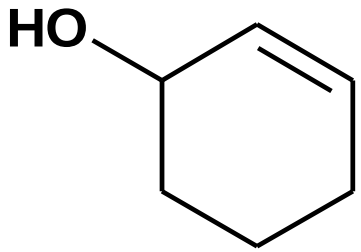
notice the removal of the (e)

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.

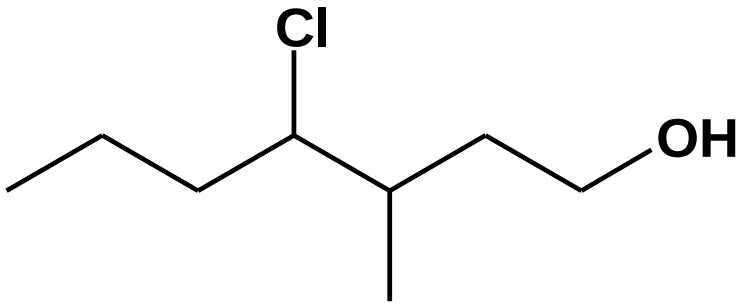
e.g.



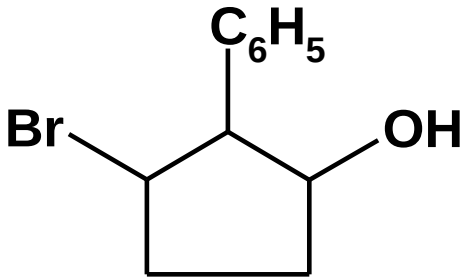
3-Ethyl-3-buten-2-ol



2-Cyclohexenol

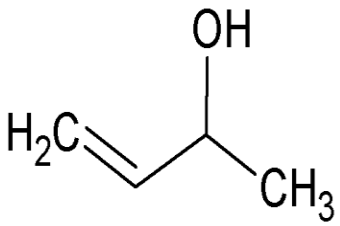


4-Chloro-3-methyl-heptan-1-ol

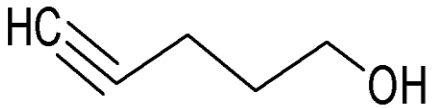


3-Bromo-2-phenyl cyclopentanol

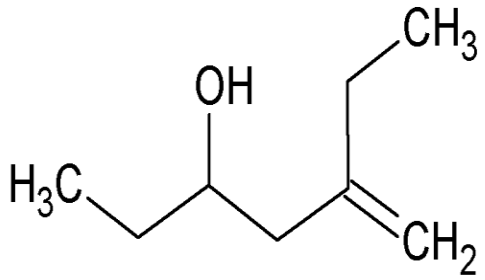
3-Butyn-2-ol



3-buten-2-ol



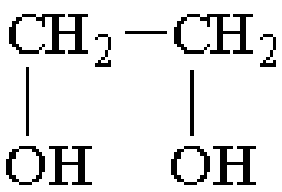
4-Pentyn-1-ol

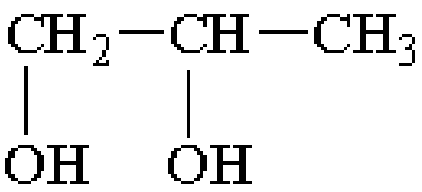


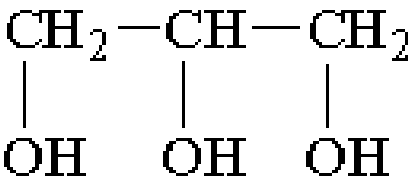
5-Ethyl-5-hexen-3-ol

- 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.



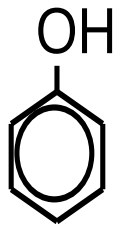




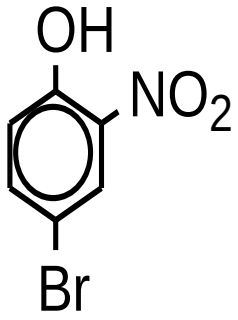
IUPAC	**1,2-Ethanediol**	**1,2-Propanediol**	**1,2,3-Propanetriol**
Common	**Ethylene glycol**	**propylene glycol**	**glycerol** or **glycerin**

Nomenclature Of Phenols

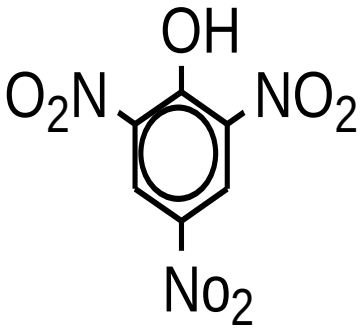
- Compounds that have a hydroxyl group attached directly to a ***benzene ring are*** called **phenols.**
- The *ortho*, *meta*, *para* system is used in common names.
- While the numbering system is employed in IUPAC names and in this case numbering of the ring begins at the hydroxyl-substituted carbon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



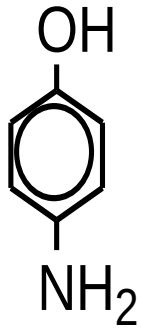
Phenol



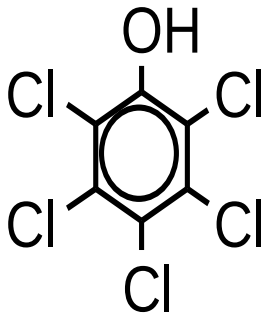
4-Bromo-2-nitrophenol



2,4,6-Trinitrophenol



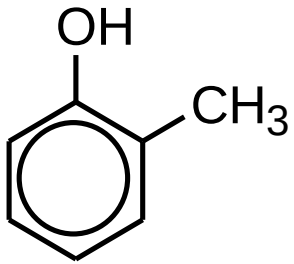
4-Aminophenol

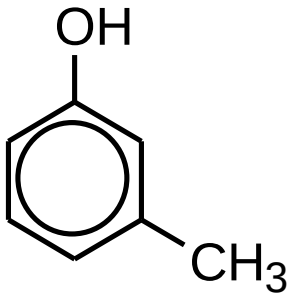


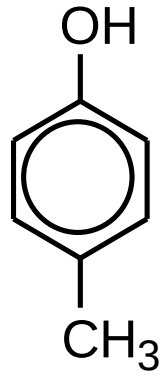
2,3,4,5,6-Pentachlorophenol

Common name: Picric acid

➢Some phenols have common names as shown in the following examples



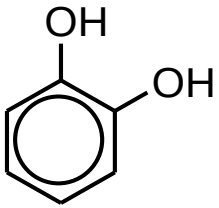


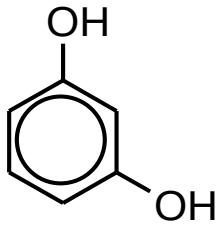


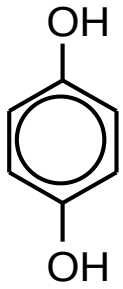
IUPAC: 2-Methyl-phenol
Common: *o*-Cresol

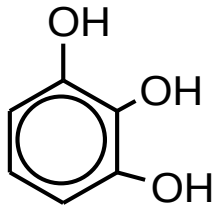
3-Methyl-phenol
m-Cresol

4-Methyl-phenol
p-Cresol









IUPAC: 2-Hydroxyphenol or 1,2-Benzenediol
Common: Catechol

3-Hydroxyphenol
Resorcinol

4-Hydroxyphenol
Hydroquinone

2,3-Dihydroxyphenol
Pyrogallol

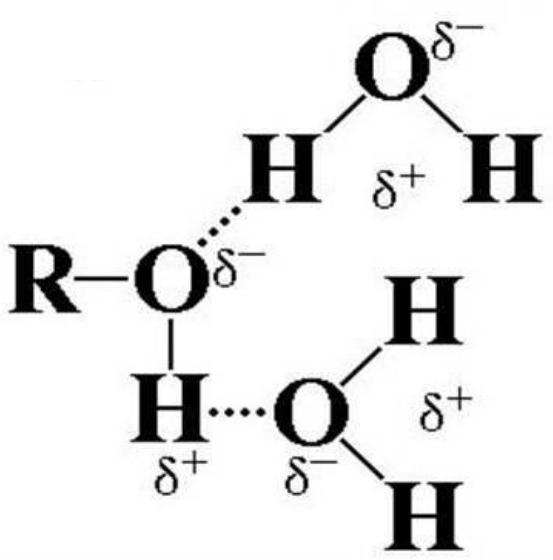
Physical Properties of Alcohols & Phenols

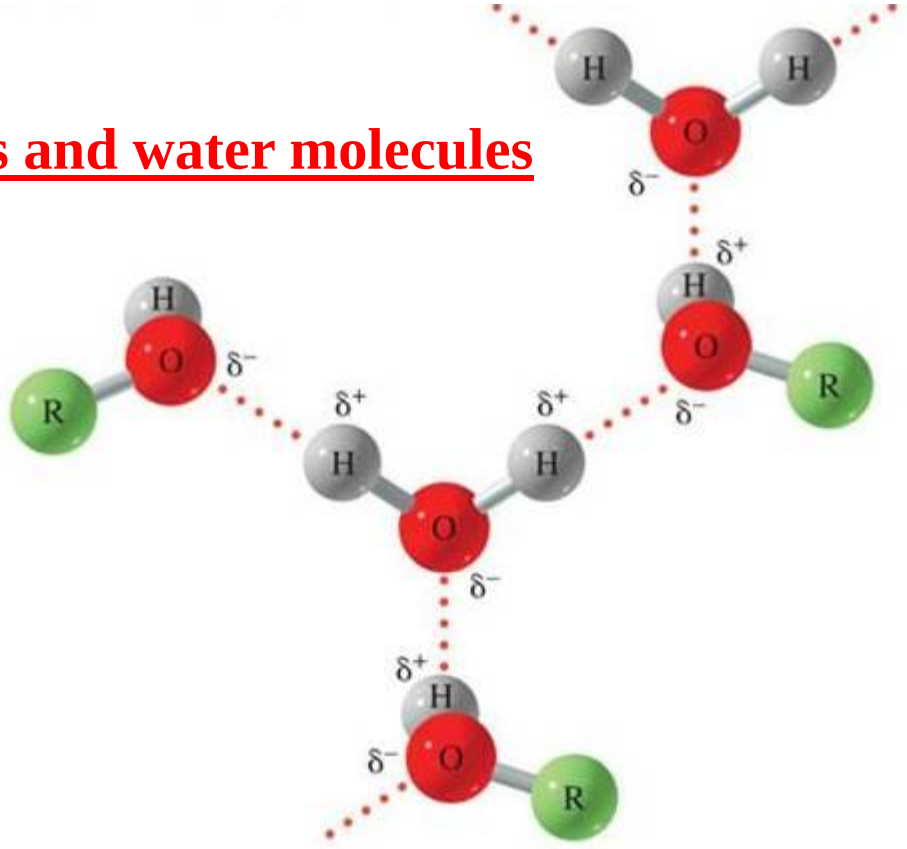
- The lower members of alcohols are colorless, volatile liquids with a characteristic alcoholic smell and burning taste whereas ***higher alcohols*** are odorless and tasteless.
  Higher alcohols having 12 or more carbon atoms are colorless waxy solids.
- Phenols are colorless, crystalline solids or liquids.

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

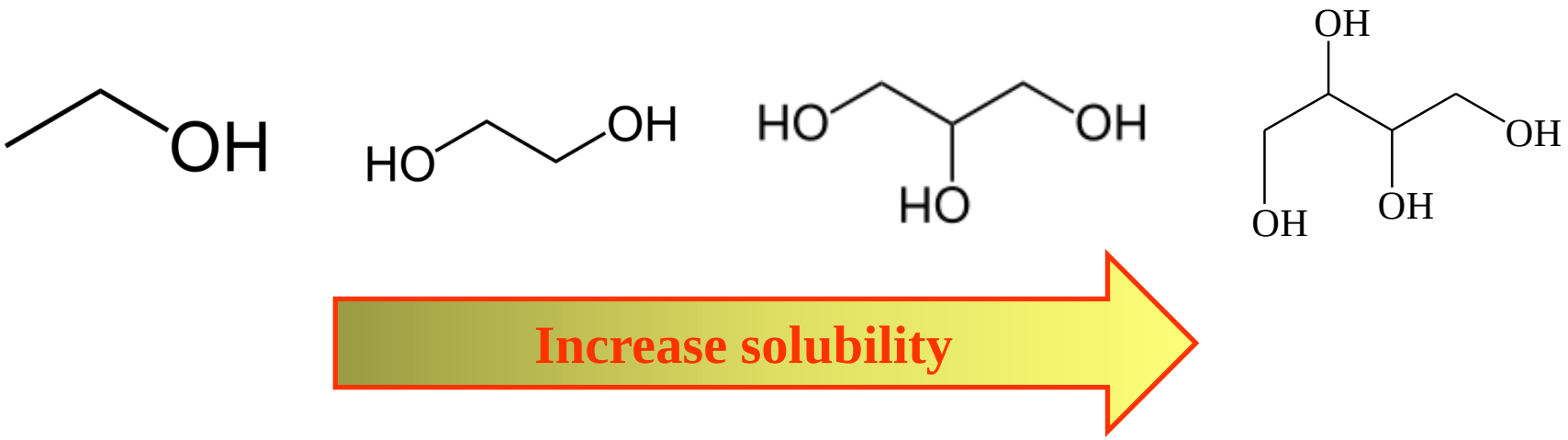
•The solubility of lower alcohols is due to the existence of hydrogen bonds between water and polar -OH group of alcohol molecules. **Phenols** too are sparingly soluble in water. The -OH group in alcohols and phenols contain a hydrogen bonded to an electronegative oxygen atom. Thus they form hydrogen bonds with water molecules.

Hydrogen bonding between alcohols and water molecules

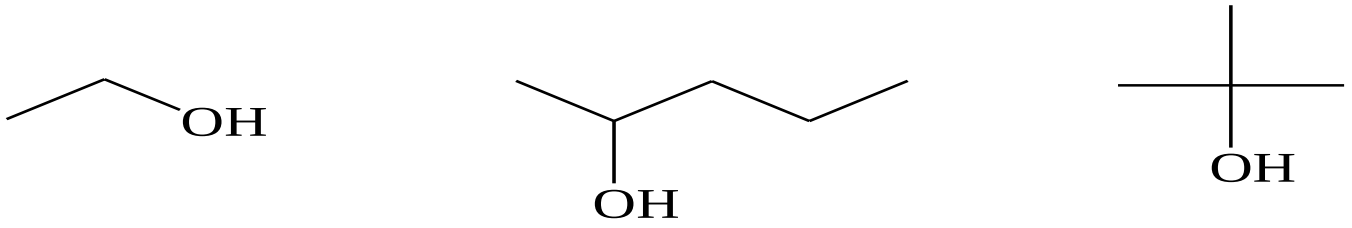




•The number of hydroxyl groups **increases** the solubility.



•The solubility increases with branching of chain.

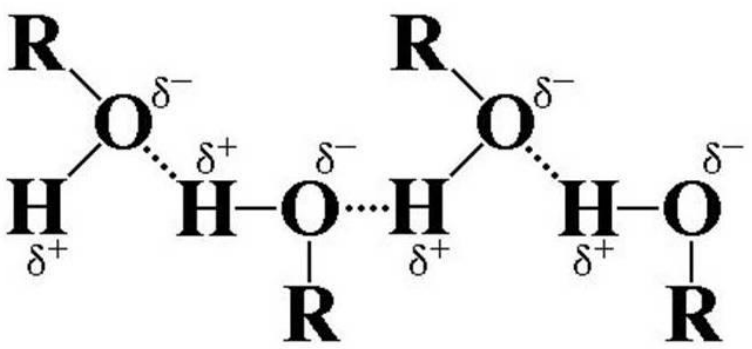


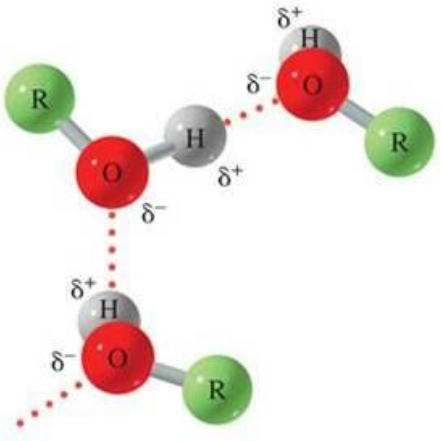
• Phenols are sparingly soluble in water but readily soluble in organic solvents ..

• **Boiling points of alcohols** Boiling point of alcohols are much higher than those of alkenes, halo alkenes or ethers of comparable molecular masses.

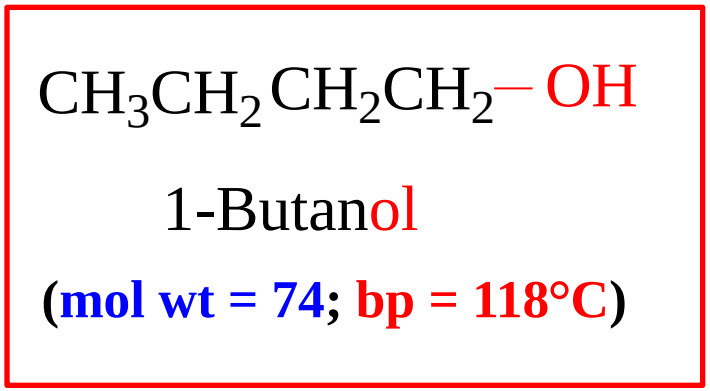
CH_3CH_2-OH	$CH_3CH_2CH_3$	CH_3-O-CH_3
Eyhanol	*n*-propane	Dimethylether
Mol wt = 46; bp= 78°C	Mol wt = 44; bp= -42°C	Mol wt = 46; bp= -24°C

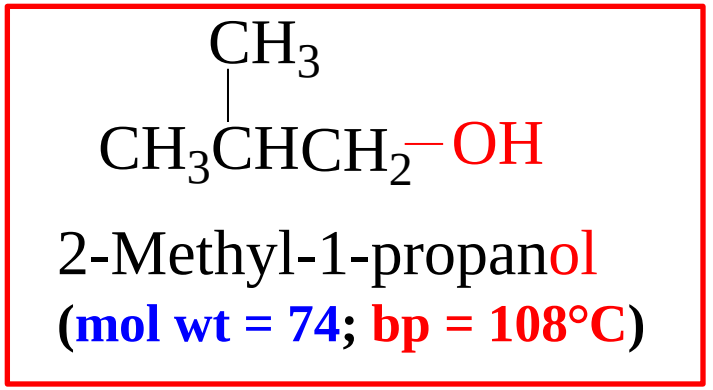
•This is because in alcohols intermolecular hydrogen bonding exists due to which a large amount of energy is required to break these bonds.

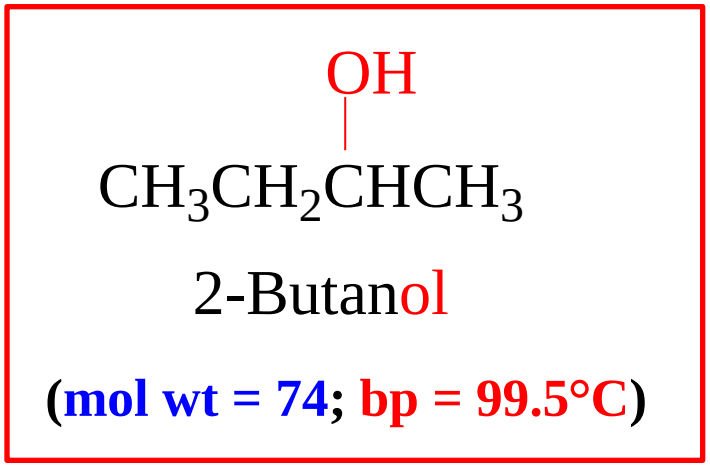


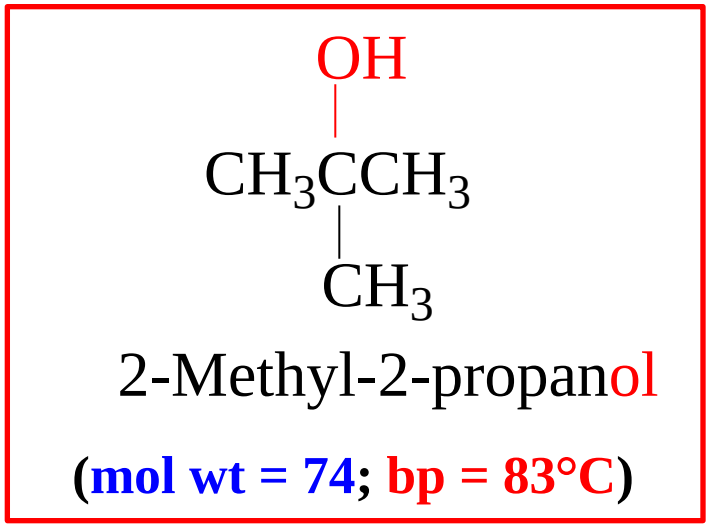


• Among isomeric alcohols, the boiling point decreases with increase in branching in the alkyl group.









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

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

Acidity of Alcohols & Phenols

- Due to the electronegativity of the O atoms, alcohols are ***slightly*** acidic (pKa 16-18)

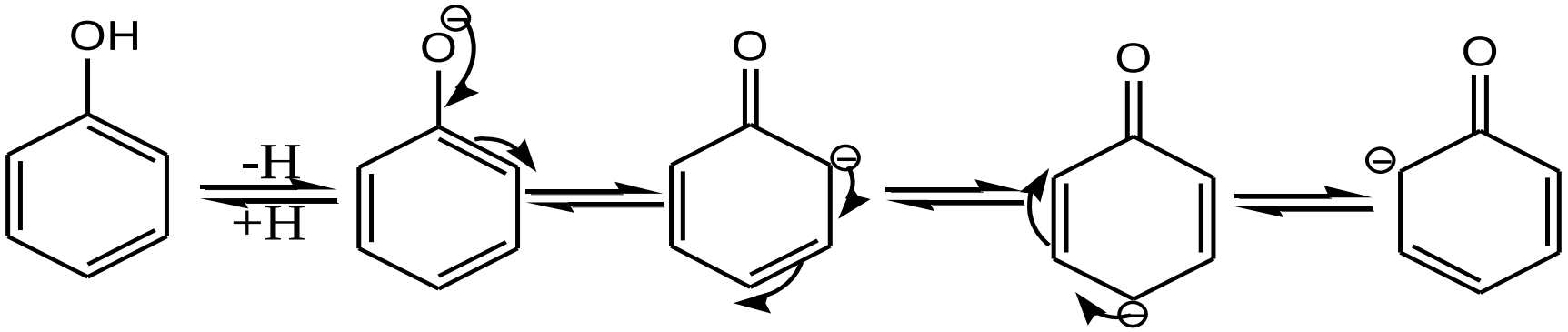
- The anion derived by the deprotonation of an alcohol is the **alkoxide**.

- Alcohols and phenols have **weak acidic properties**.

- Phenols are **much stronger acids** than alcohols.

Why ??

Because the negative charge in oxygen is dispersed by resonance through the benzene ring.



Resonance structures of phenoxide anion

Effect of substituents on the acidity of phenols

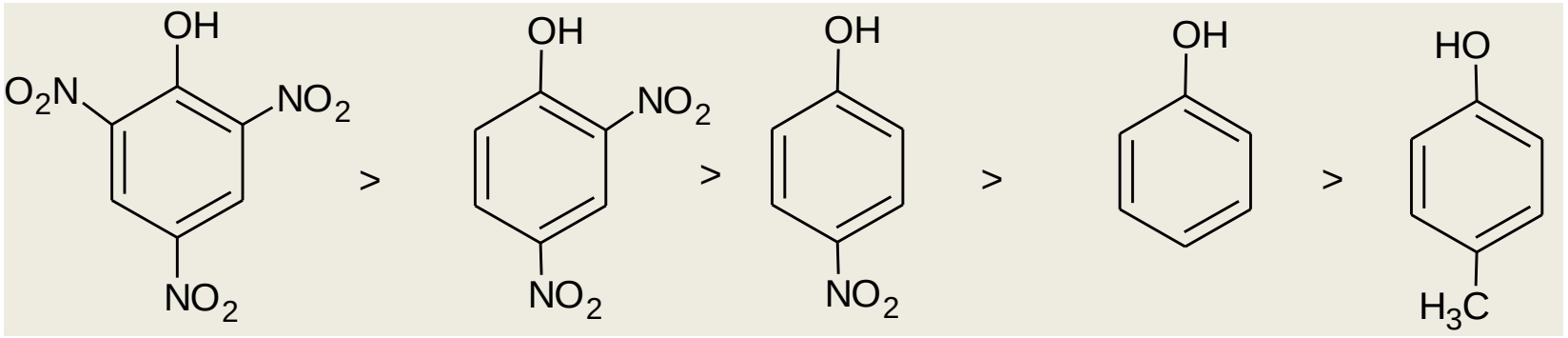
- Introduction of electron-withdrawing groups (EWG), such as NO_2 or CN, X on the ring ***increases the acidity*** of phenol.

- Also, introducing electron-donating groups (EDG), such as NH_2, R, OR ***decrease the acidity*** of phenols.

- The electron donating or withdrawing effect is generally more pronounced if **the substituted** is present at o- and p- position.

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

Acidity order



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

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

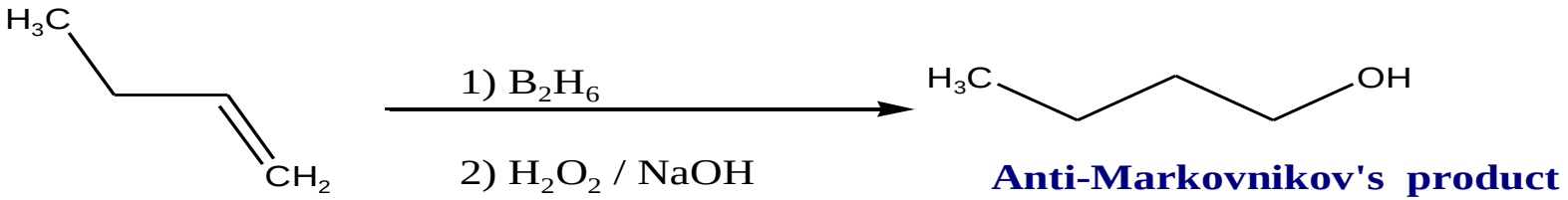
(b) *o*-Iodophenol or *p*-Iodophenol

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

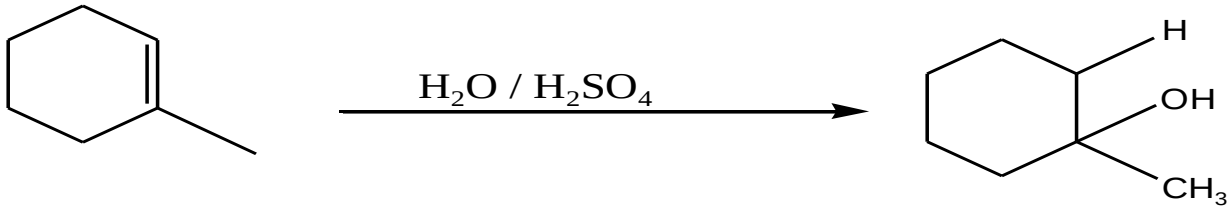
(d) *o*-Nitrophenol or *m*-Nitrophenol

A. Preparation of alcohols:

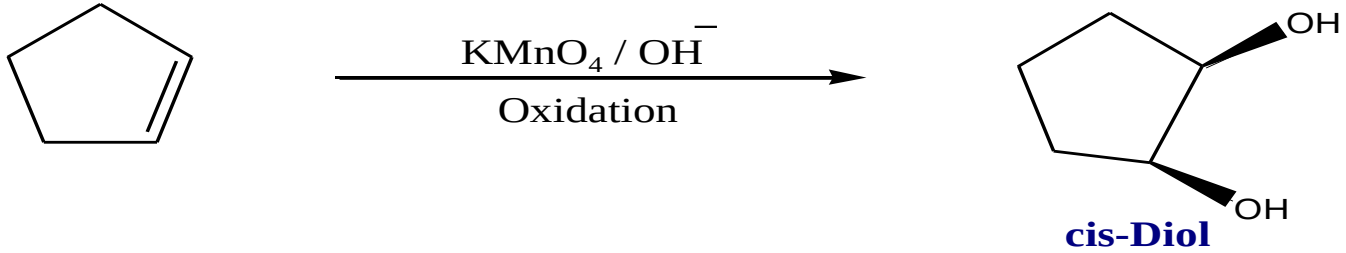
1- From alkenes



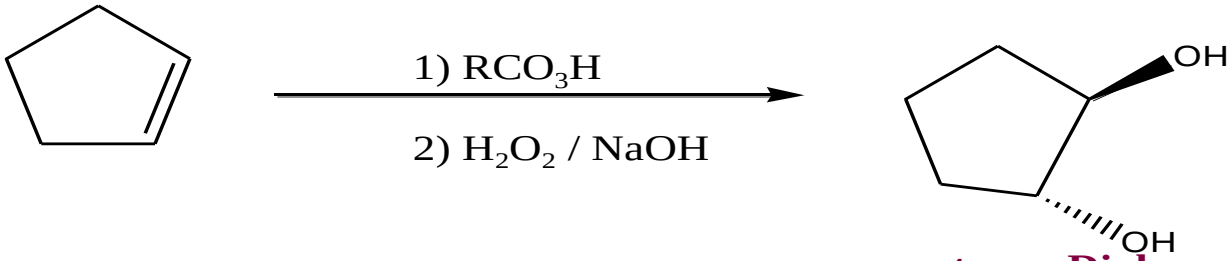
Anti-Markovnikov's product



Markovnikov's product

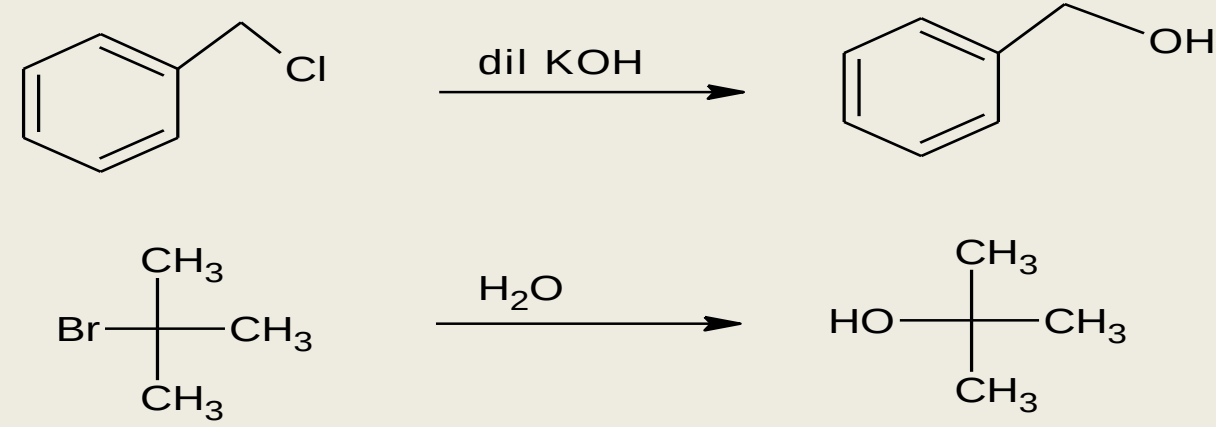


cis-Diol

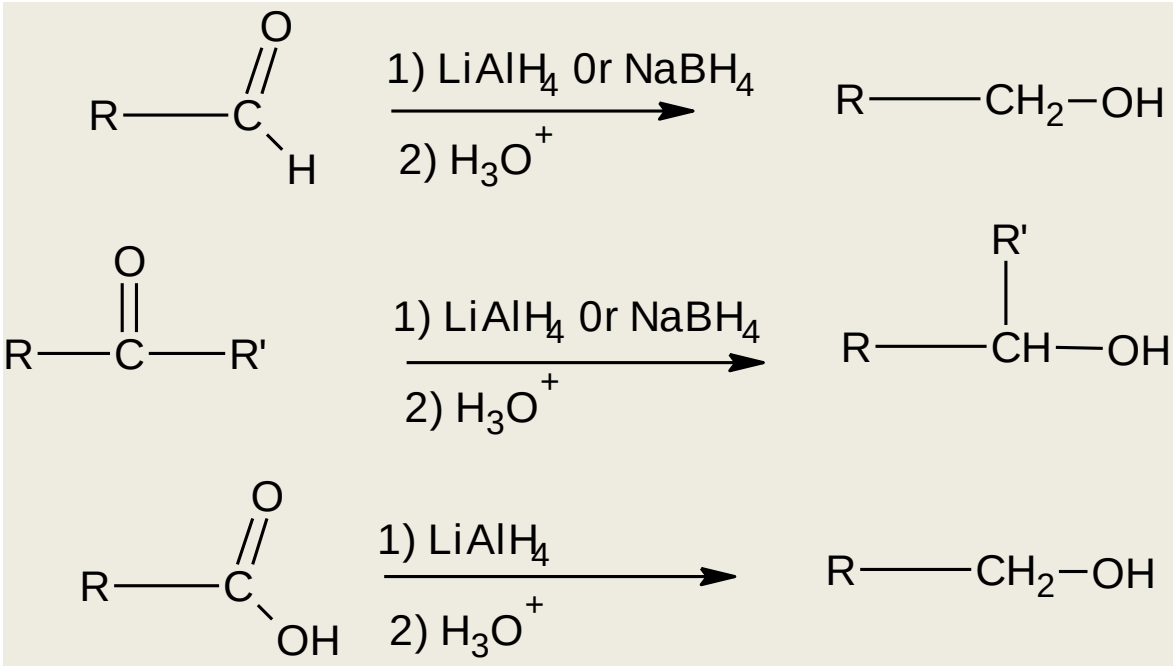


trans-Diol

2- From alkyl halide

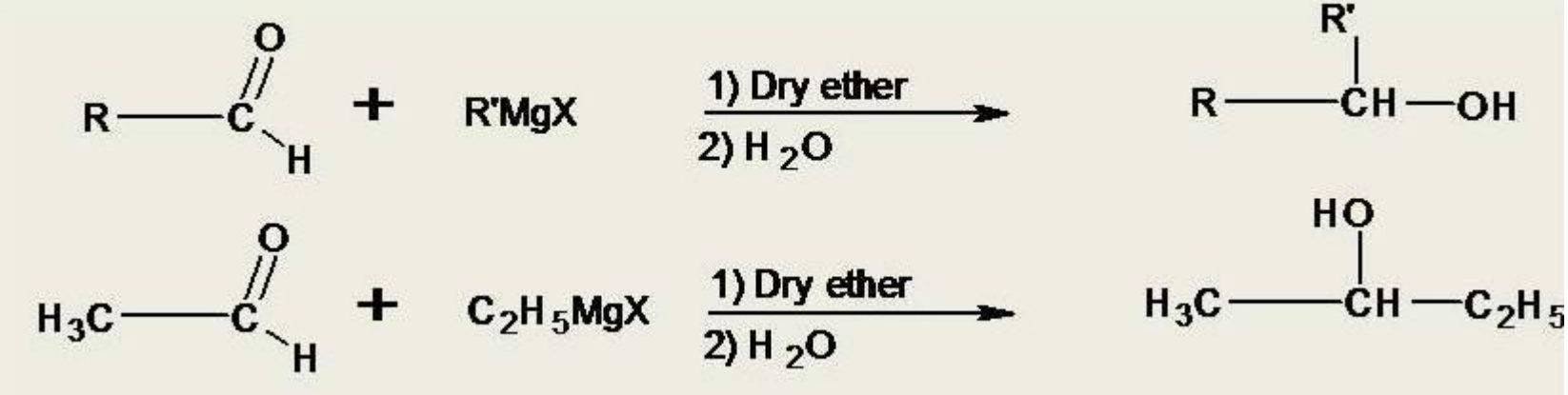


3- From aldehyde, ketone and carboxylic acid (Reduction reaction)

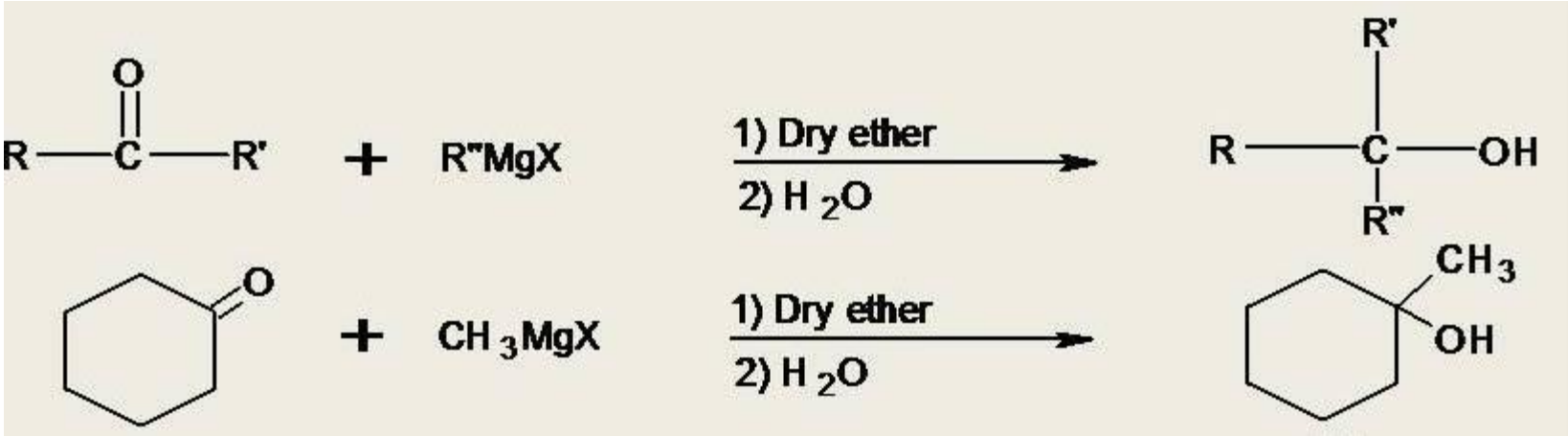


4- From Grignard reagent

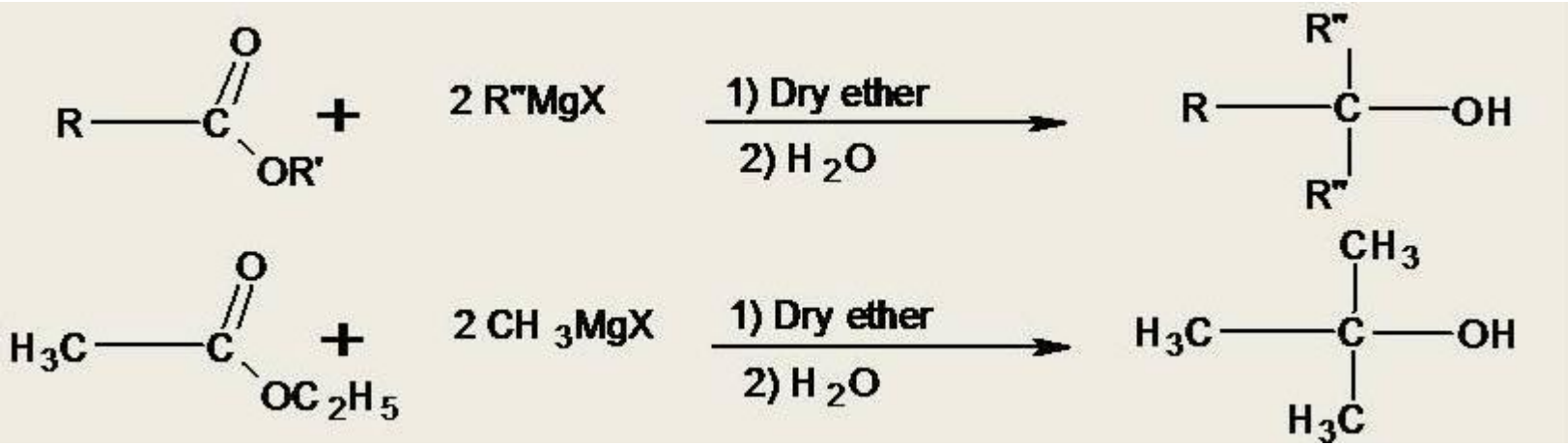
Reaction with Aldehyde



Reaction with ketone

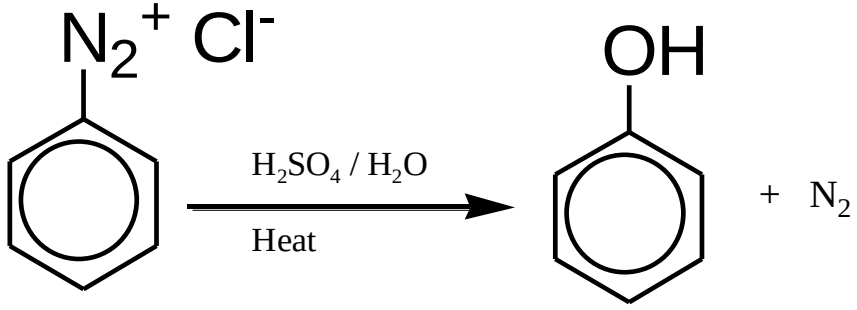


Reaction with Ester

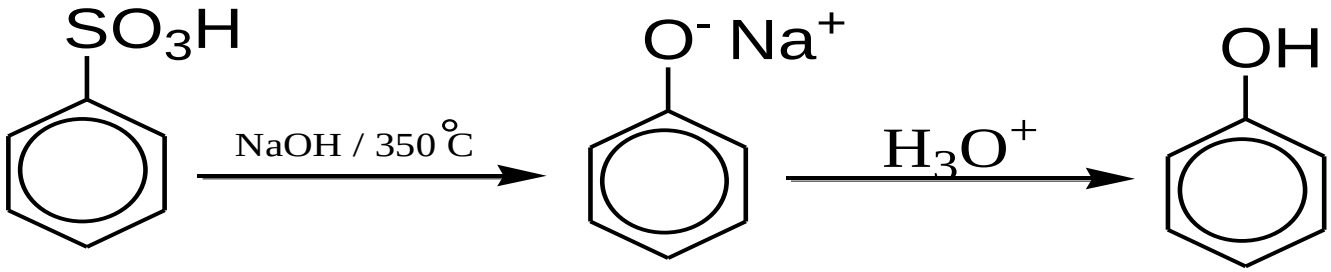


Preparation of Phenols

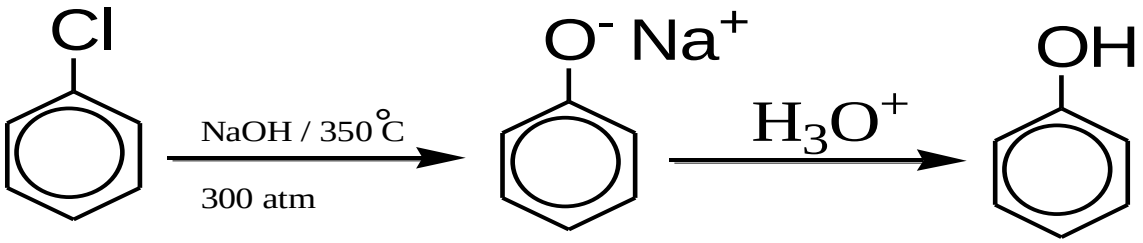
1- Hydrolysis of Diazonium salts



2- Fusion of sodium with benzene-sulfonates:

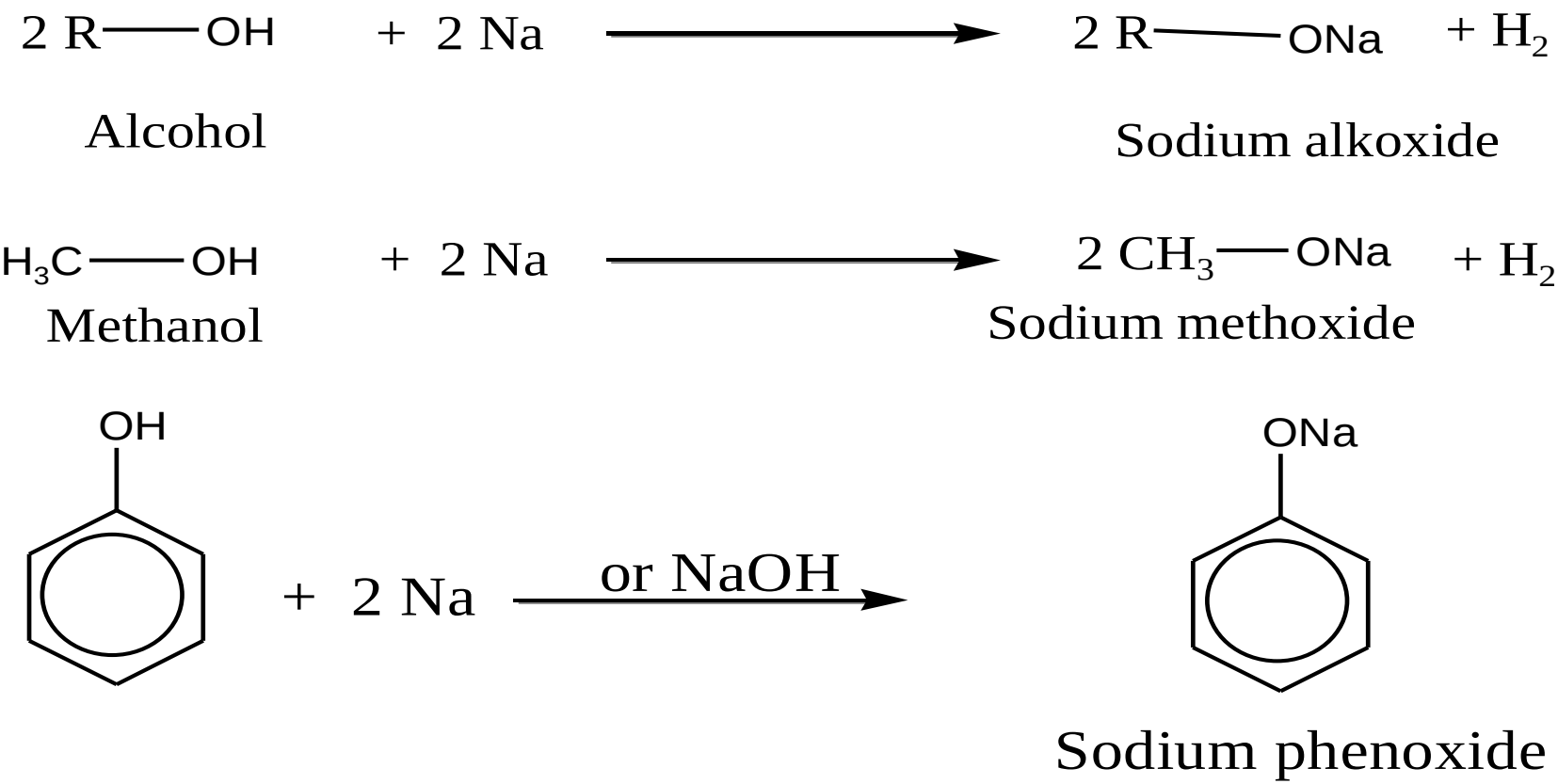


3- From alkyl halide:



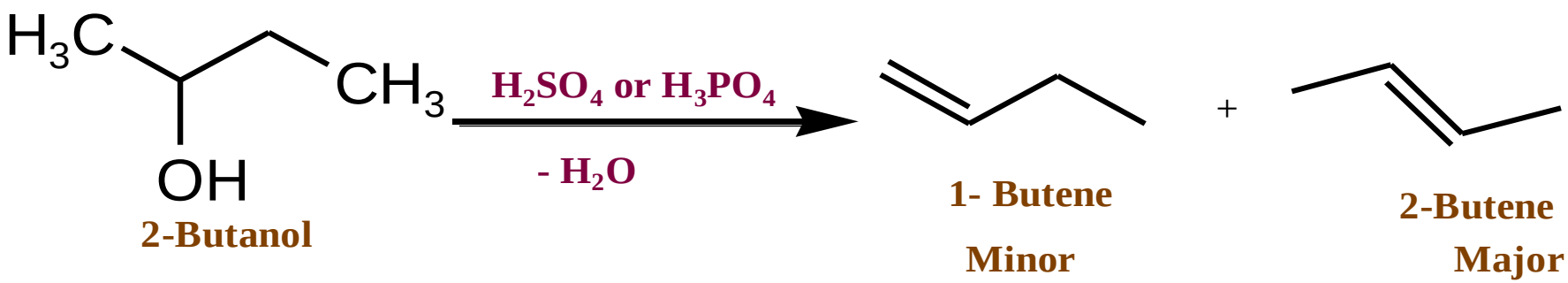
Reaction of Alcohols and Phenols

1) Salt Formation By Reaction With Active Metals

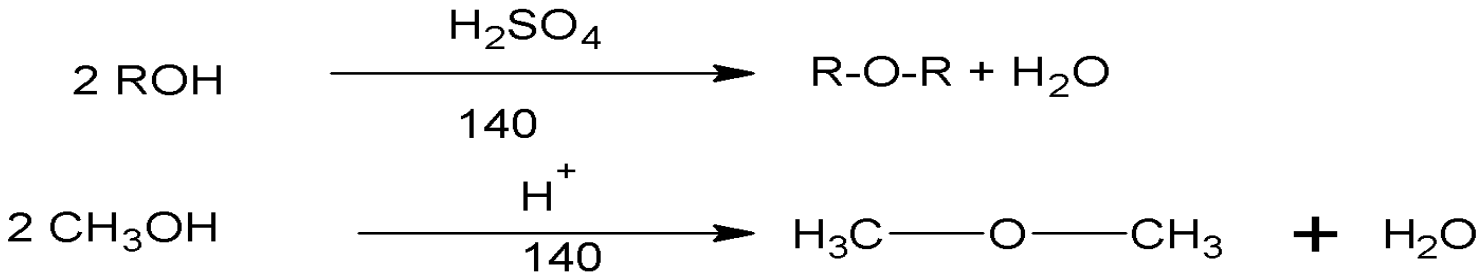


2) Elimination Of Water (Dehydration)

Reagent/catalyst conc. sulphuric acid (H_2SO_4)
Conditions reflux at 180°C
Product alkene

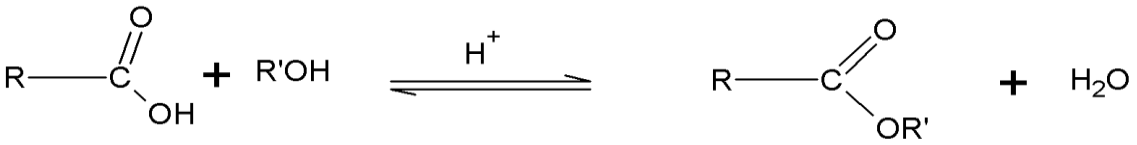


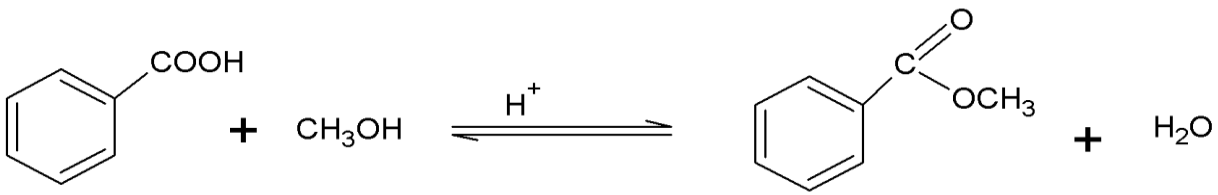
While dehydration of alcohols at lower temperature will give ethers



3) Ester Formation

- **Carboxylic acid + alcohol in presence of strong acid catalyst (e.g. conc. H_2SO_4) produces esters**





4) Alkyl Halides Formation

$$R{-}OH + HX \xrightarrow{ZnCl_2} R{-}X + H_2O$$

$$R{-}OH + SOX_2 \longrightarrow R{-}X + SO_2 + HCl$$

$$R{-}OH + PX_3 \longrightarrow R{-}X + HOPX_2$$

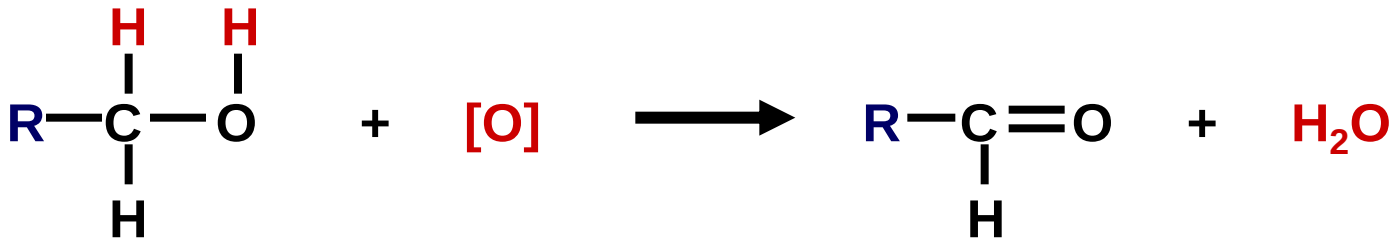
$$R{-}OH + PX_5 \longrightarrow R{-}X + HOPX_4$$

5) Oxidation Of Alcohols

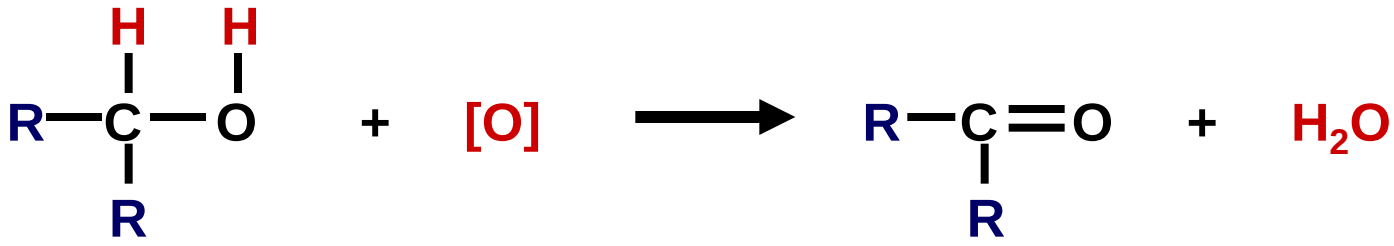
Alcohols can be oxidised depending on their class

- For oxidation to take place easily you must have two hydrogen atoms on adjacent C and O atoms.

1°

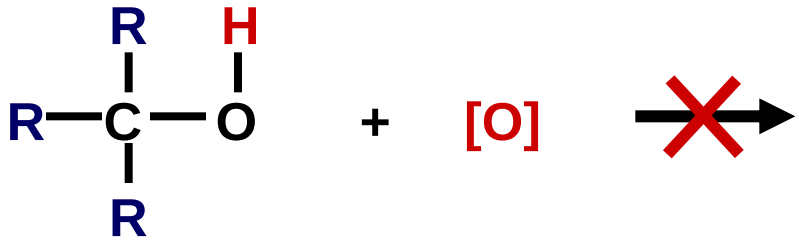


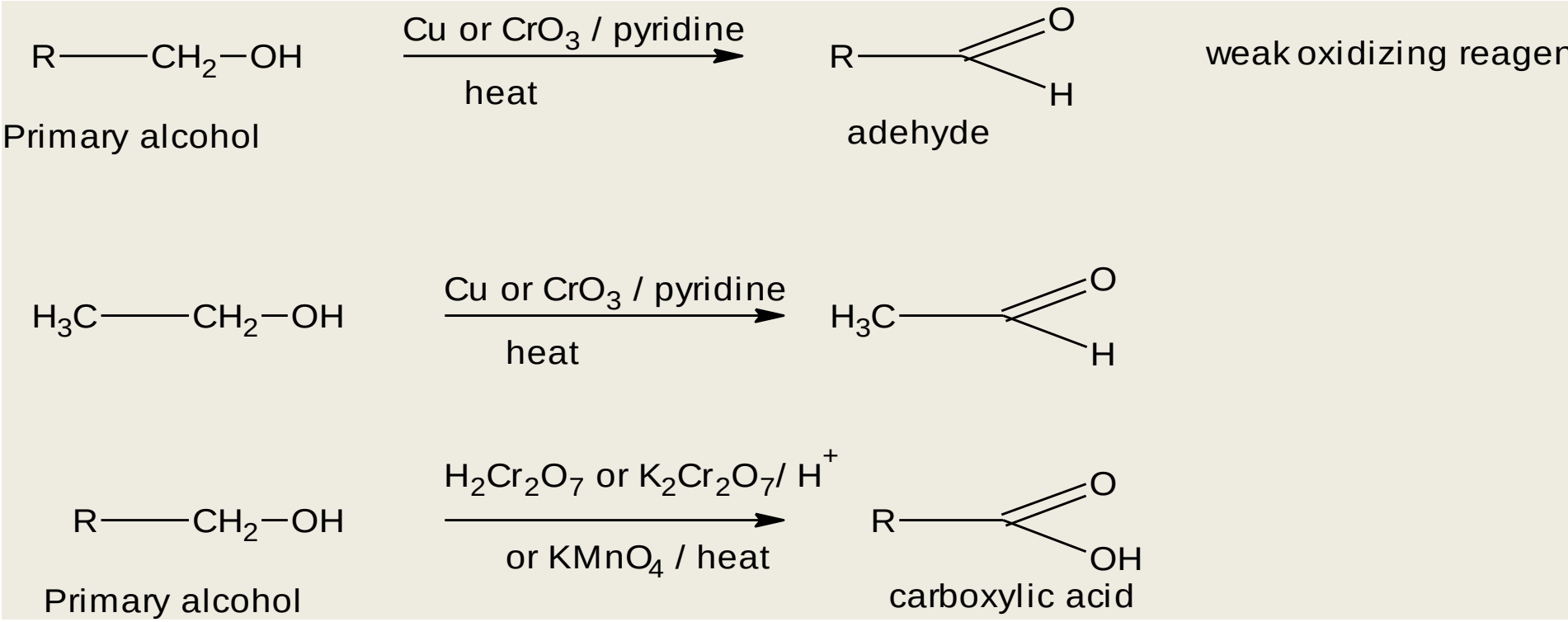
2°

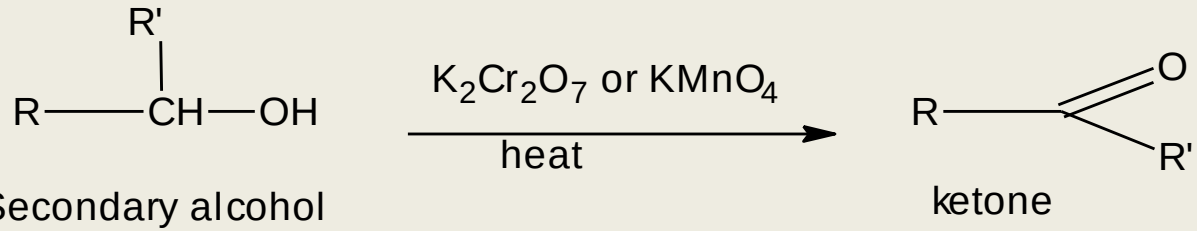


This is possible in 1° and 2° alcohols but not in 3° alcohols.

3°

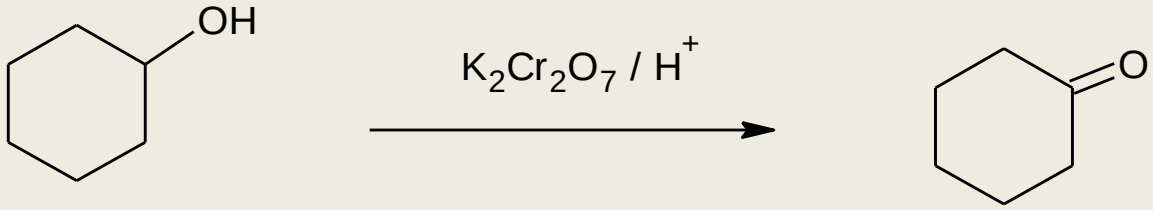


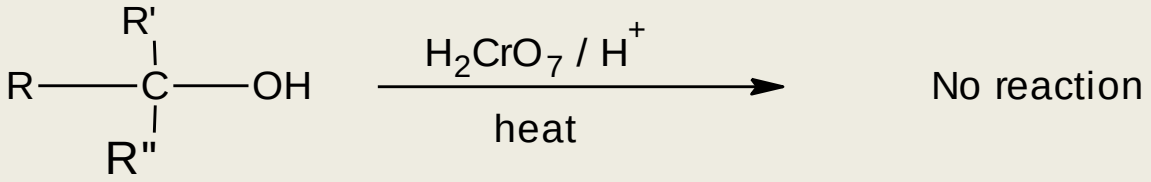

R——CH2—OH
Cu or CrO3 / pyridine
heat
O
R
H
weak oxidizing reagen
Primary alcohol
adehyde
H3C——CH2—OH
Cu or CrO3 / pyridine
heat
O
H3C
H
R——CH2—OH
H2Cr2O7 or K2Cr2O7/ H+
or KMnO4 / heat
O
R
OH
Primary alcohol
carboxylic acid



Secondary alcohol

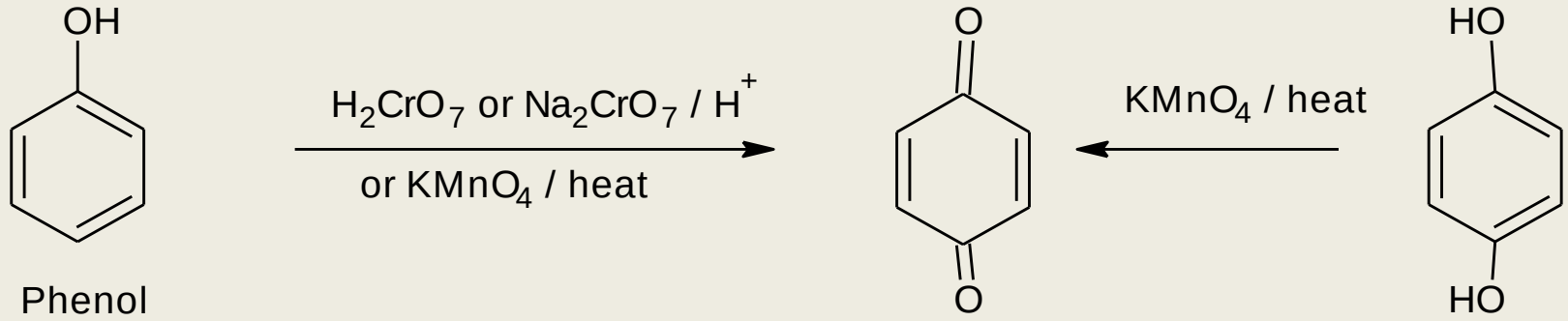
ketone





Tertiary alcohol

No reaction

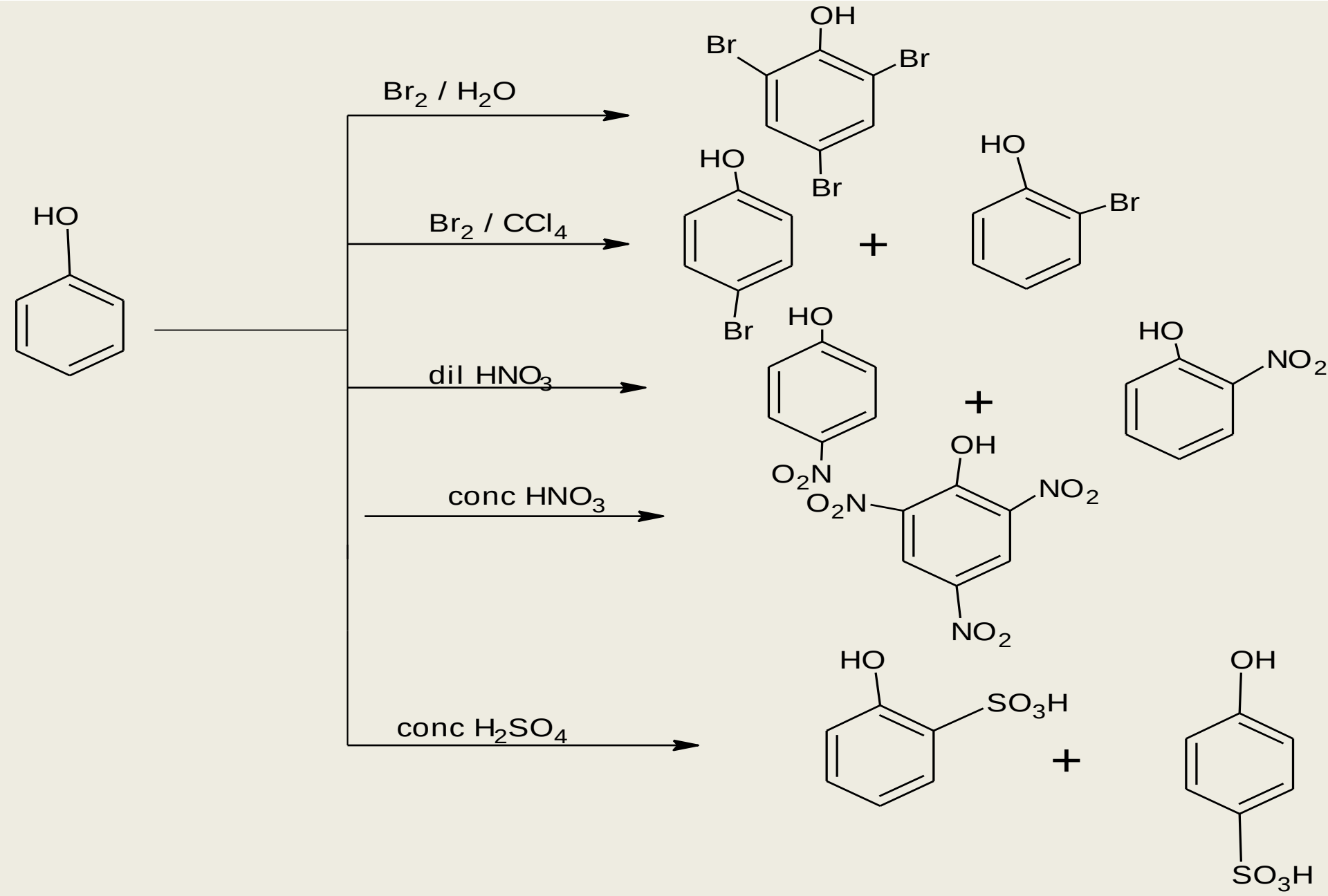


Phenol

p-Benzoquinone

Hydroquinone

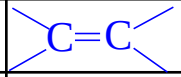
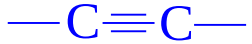
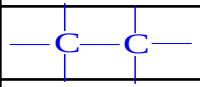
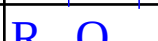
6- Reaction of aromatic ring of phenols



Functional Group Precedence in IUPAC nomenclature

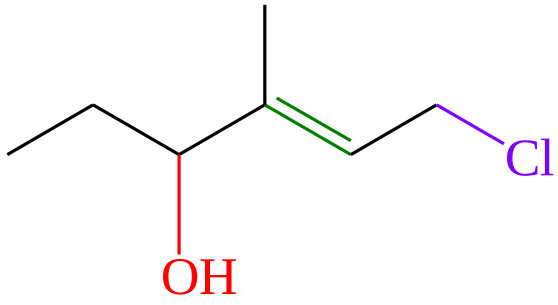
When two or more functional groups are present in a molecule, that group highest in the table is used as the parent (suffix) in the IUPAC name and all others are cited as substituents (prefixes).

Priority Order

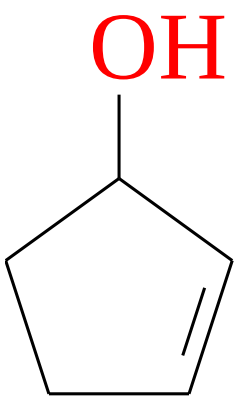
	Function Group Name	Formula	Suffix	Prefix
1-	Carboxyl	-COOH	carboxy-	-oic acid
2-	Ester	-COOR	R-oxycarbonyl-	-R-oate
3-	Aldehyde	-CHO	Formyl-	-al
4-	Ketone	>C=O	oxo-	-one
5-	Alcohol	-OH	hydroxy-	-ol
6-	Amine	$-NH_2$	Amino-	-Amine
7-	Alkene		----------	-ene
8-	Alkyne		----------	-yne
9-	Alkane		Alkyl-	----------
10-	Ethers		Alkoxy-	----------
11-	Halides	F, Cl, Br, I-	Halo-	----------

Examples

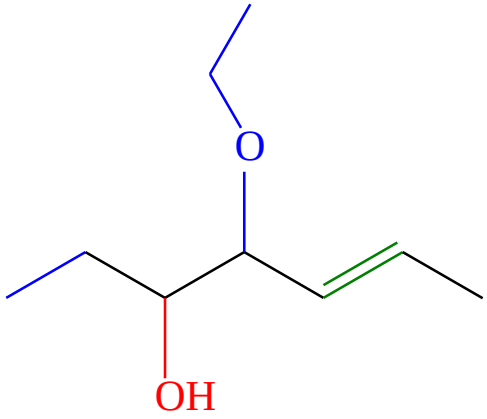
3-pentene-1-yne



6-chloro-4-methyl-hexa-4-en-3-ol



2-cyclopen-1-ol



4-Ethoxyhept-5-en-3-ol

H.W(6)

Page: 187; problems 7.12

Page: 194; problem 7.18