PHA284

Organic Chemistry II

Ankara University
Faculty of Pharmacy
Department of Pharmaceutical Chemistry

ALCOHOLS

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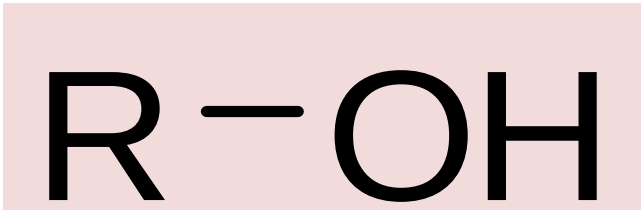
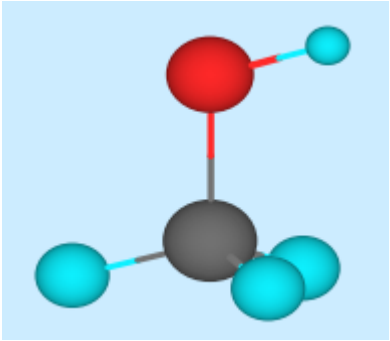
The word alcohol immediately brings to mind ethanol, the intoxicating compound in wine and beer.

The functional group of an alcohol is an -OH group bonded to an sp^3 hybridized carbon





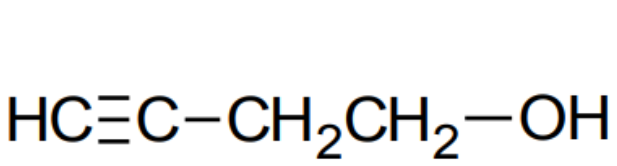
Methanol

Nomenclature

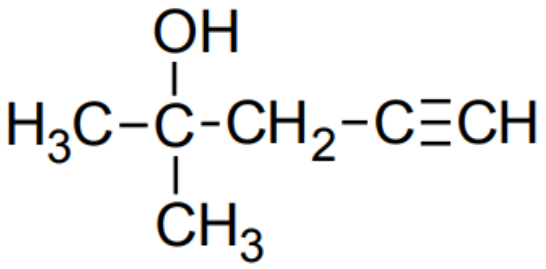
methanol
(methyl alcohol)

ethanol
(ethyl alcohol)

1-propanol
(*n*-propyl alcohol)



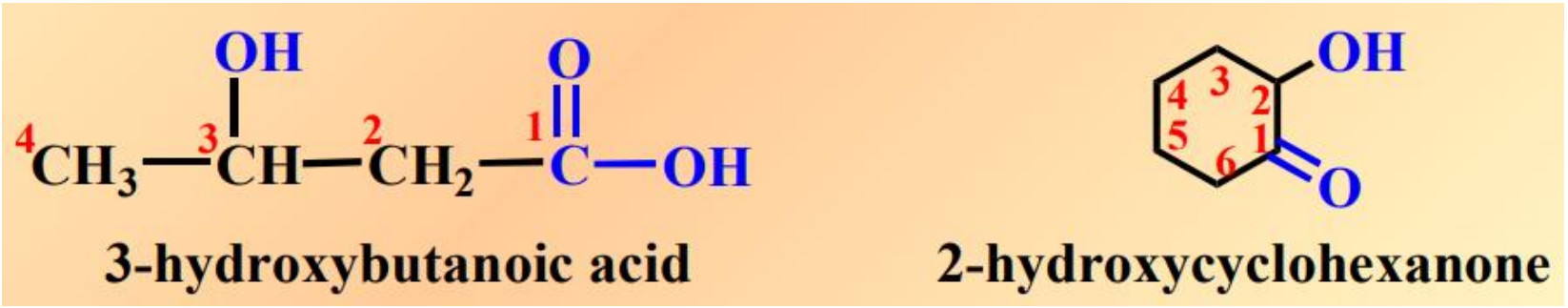
3-Butyn-1-ol



2-Methyl-4-Pentyn-2-ol

Nomenclature

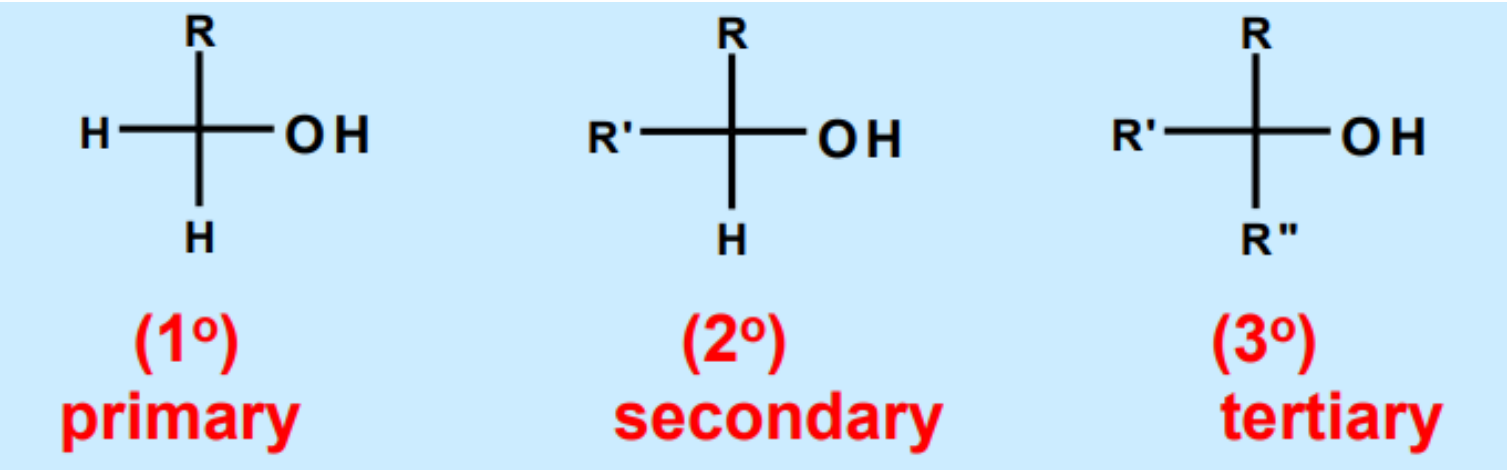
- OH functional group is named as a **hydroxy** substituent when it appears on a structure with a **higher priority functional group** such as acids, esters, aldehydes and ketones.



Classification of Alcohols

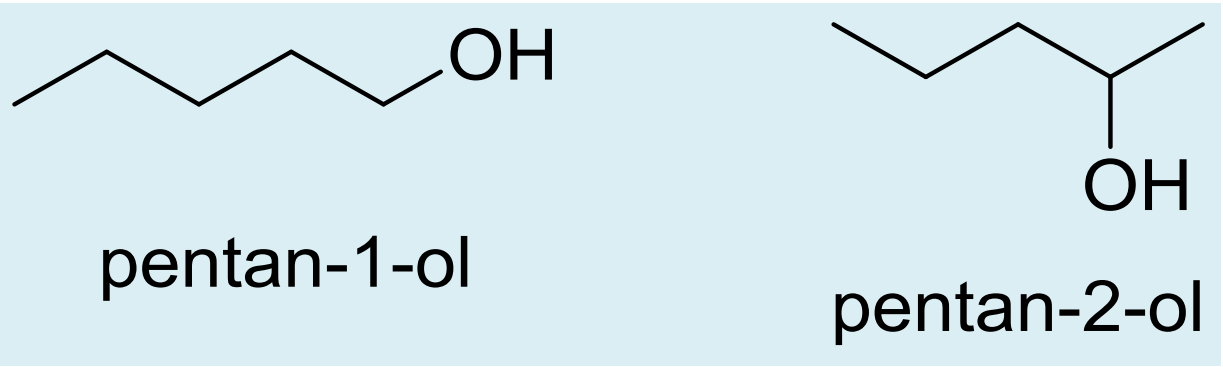
Alcohols are further classified as:

- Methyl alcohol (CH_3OH)
- primary (1^o) alcohol
- secondary (2^o) alcohol
- tertiary (3^o) alcohol



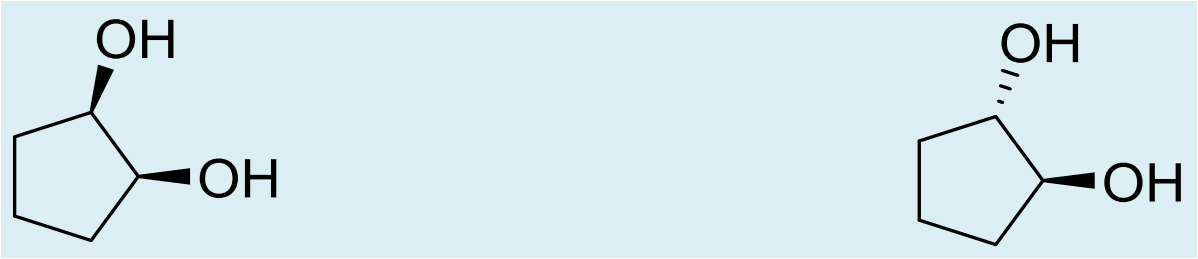
Isomerism

n-Pentyl alcohol and sec-pentyl alcohol are constitutional isomers. They have the same molecular formula ($C_5H_{12}O$) but have different structures.



Isomerism

- Compounds with atoms connected in the same order but which differ in three-dimensional orientation, are **stereoisomers.**
- The terms “cis” and “trans” should be used to specify stereoisomeric ring structures.



cis-Cyclopentane-1,2-diol

trans-Cyclopentane-1,2-diol

Physical Properties

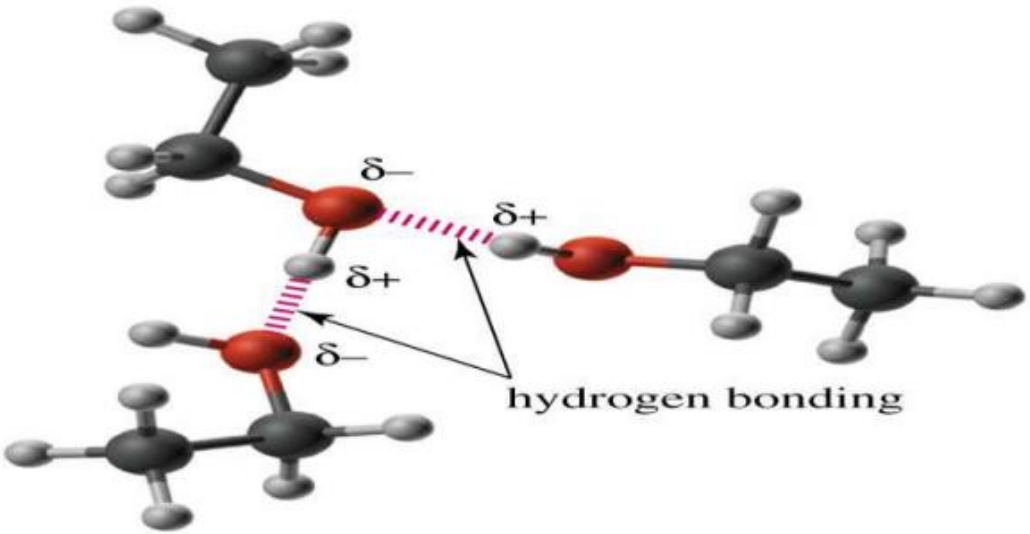
PHYSICAL STATES OF ALCOHOLS

- simple aliphatic alcohols → **liquids** at room temperature.
- highly branched alcohols and alcohols with **twelve or more** carbon atoms → **solids**.

Physical Properties

BOILING POINTS

	C_2H_5OH	$CH_3CH_2CH_3$	CH_3Cl
Relative molecular mass:	46	44	50.5
Boiling point:	78°C	-42°C	-24°C



Physical Properties

SOLUBILITY OF ALCOHOLS IN WATER

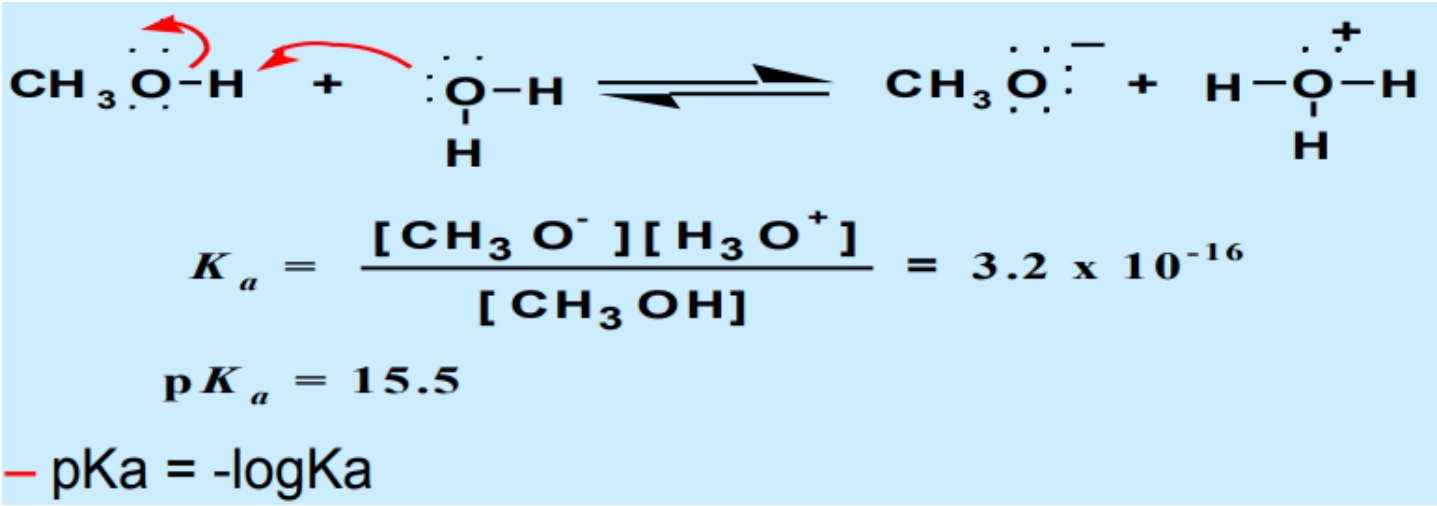
Alcohols are more soluble in water than hydrocarbons.

Higher alcohols are insoluble in water. - alcohol contains a polar end (-OH group) called '**hydrophilic**' and a non-polar end (the alkyl group) called '**hydrophobic**'.

- the water solubility decreases as the alkyl group becomes larger.

Acidity of Alcohols

- Most alcohols are about the same or slightly weaker acids than water.



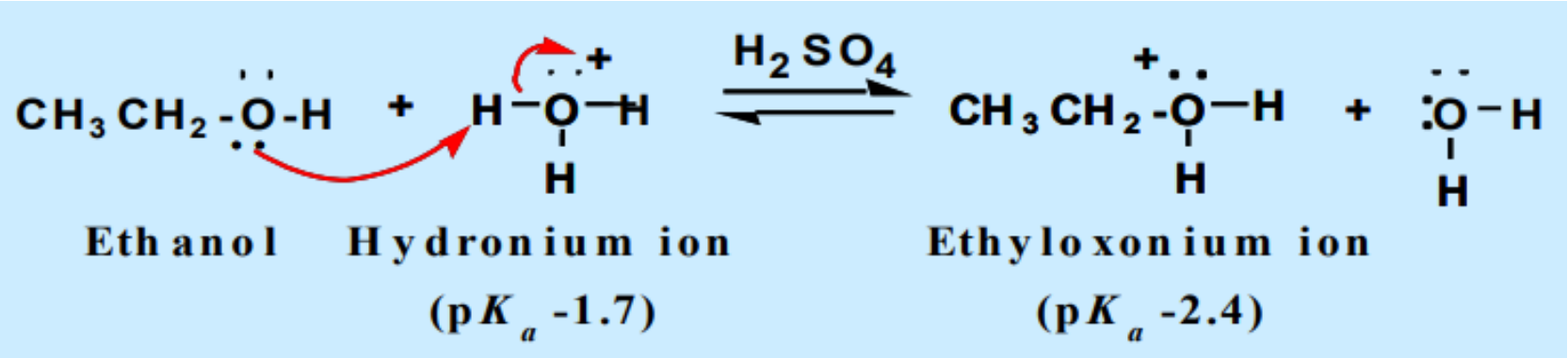
$$K_a = \frac{[CH_3O^-][H_3O^+]}{[CH_3OH]} = 3.2 \times 10^{-16}$$

$$pK_a = 15.5$$

– pKa = -logKa

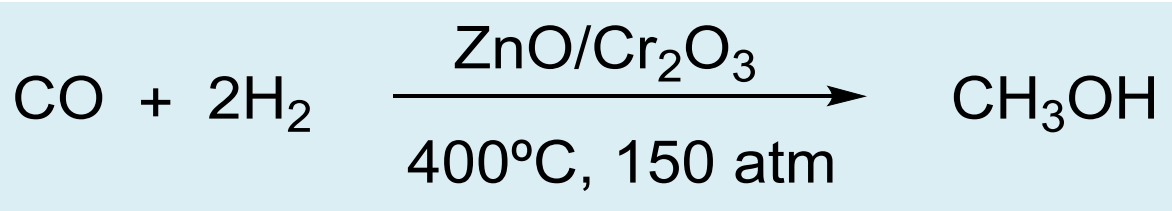
Basicity of Alcohols

Alcohols can function as both very weak acids and weak bases.



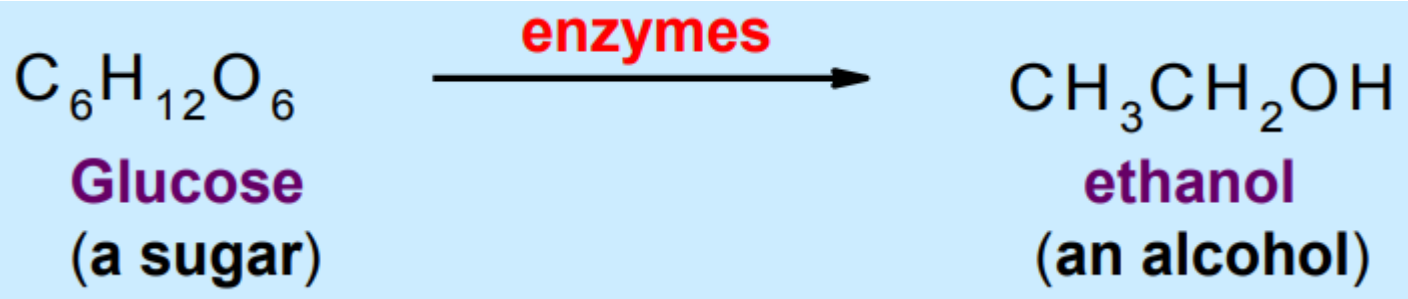
Preparation of Alcohols

Methanol is manufactured from carbon monoxide and hydrogen.



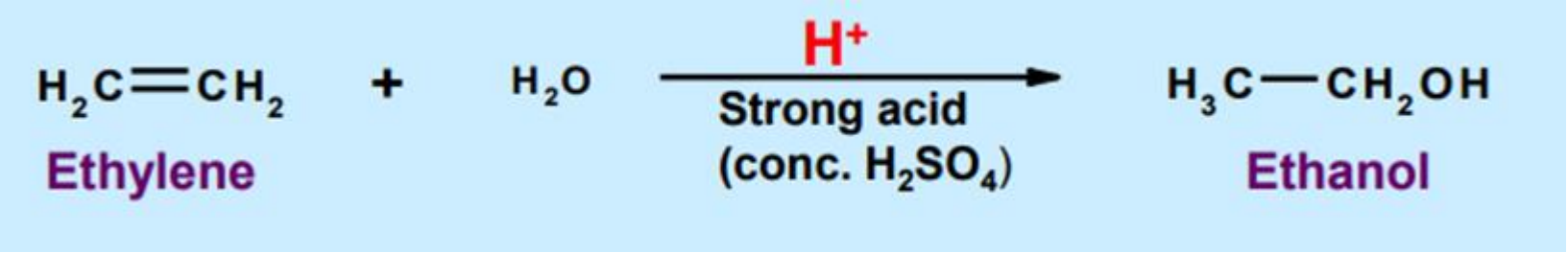
Preparation of Alcohols

i. Fermentation of carbohydrates:



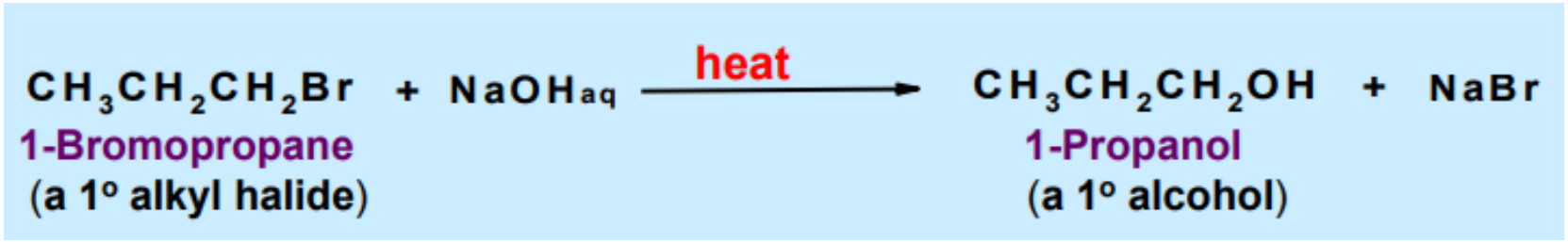
Preparation of Alcohols

ii. Hydration of alkenes:



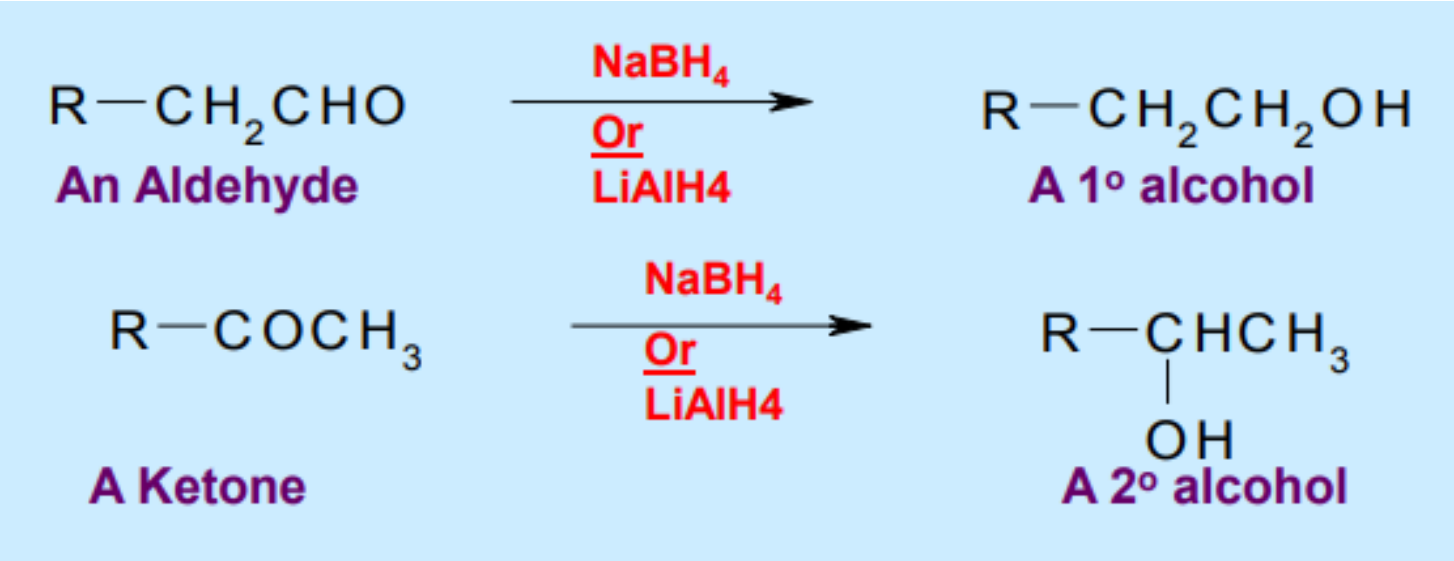
Preparation of Alcohols

iii. Nucleophilic Substitution Reactions:



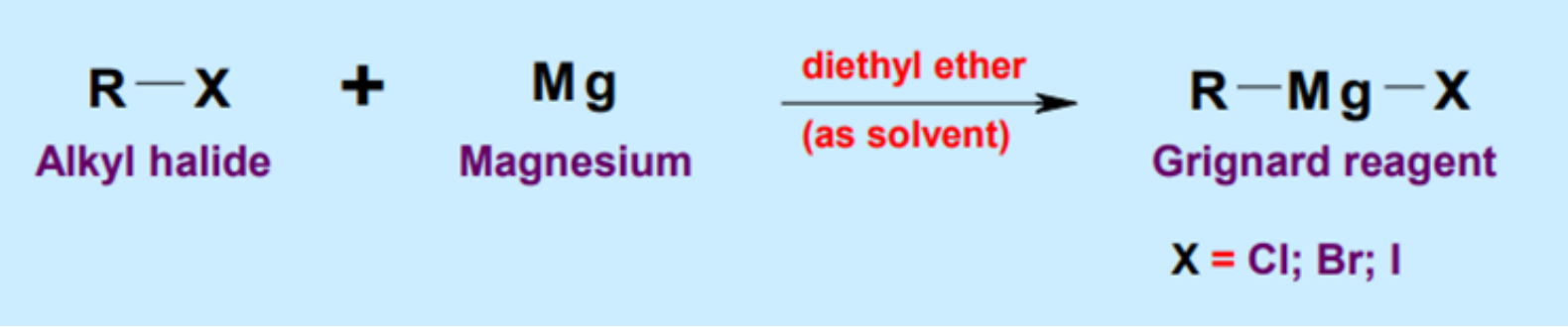
Preparation of Alcohols

iv. Reduction of Aldehydes and Ketones:



Preparation of Alcohols

v. Grignard addition to Aldehydes and Ketones:



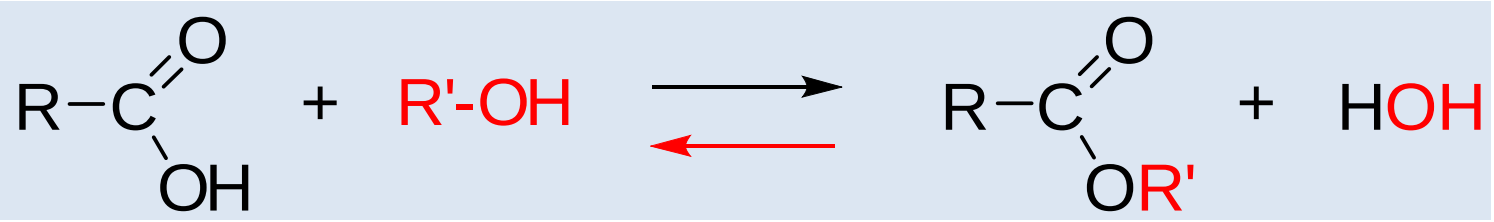
Grignard Reagents react with formaldehyde to give a 1° alcohol.

Grignard Reagents react with all other aldehydes to give 2° alcohols.

Grignard Reagents react with ketones to give 3° alcohols

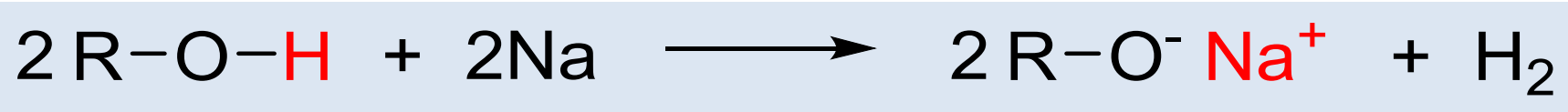
Preparation of Alcohols

vi. Ester Hydrolysis:



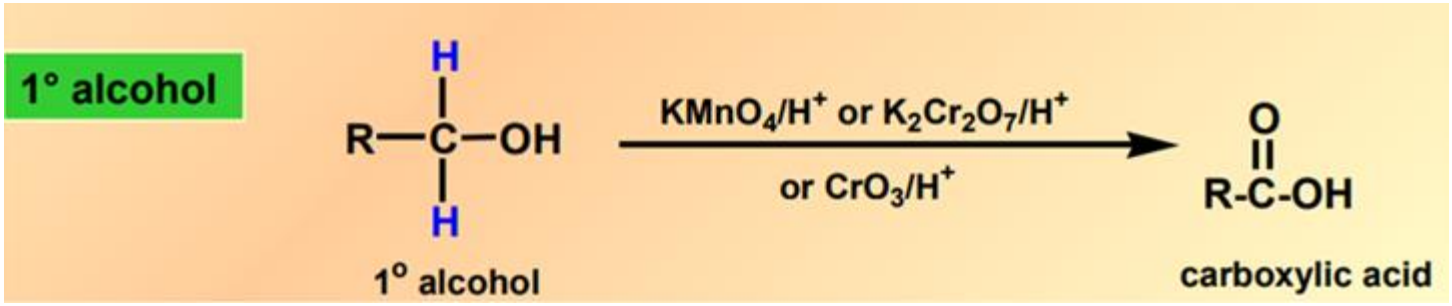
REACTIONS OF ALCOHOLS

Reaction with Sodium



REACTIONS OF ALCOHOLS

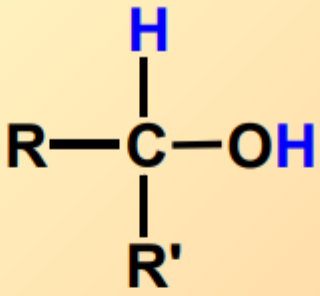
Oxidation



REACTIONS OF ALCOHOLS

Oxidation

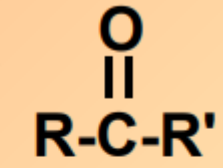
2° alcohol



2° alcohol

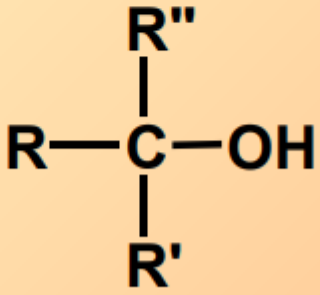
$KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$

or CrO_3/H^+



ketone

3° alcohol



3° alcohol

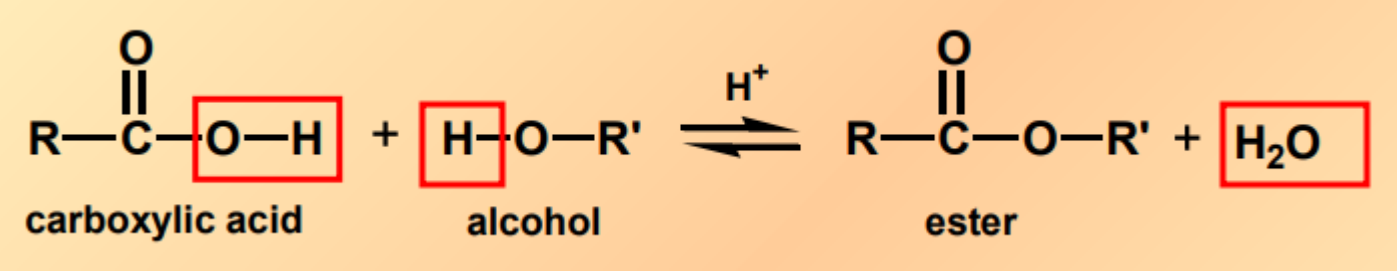
$KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$

or CrO_3/H^+

no reaction

REACTIONS OF ALCOHOLS

Esterification



REACTIONS OF ALCOHOLS

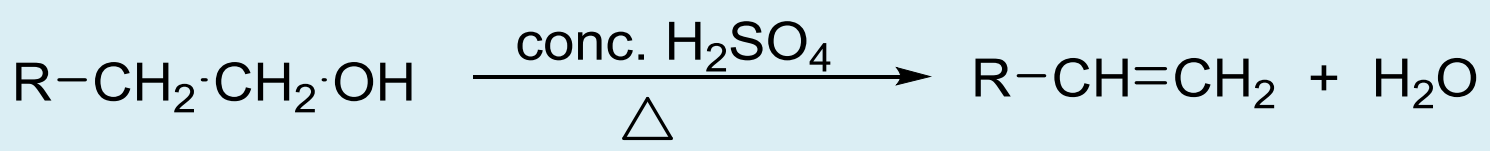
Halogenation reactions

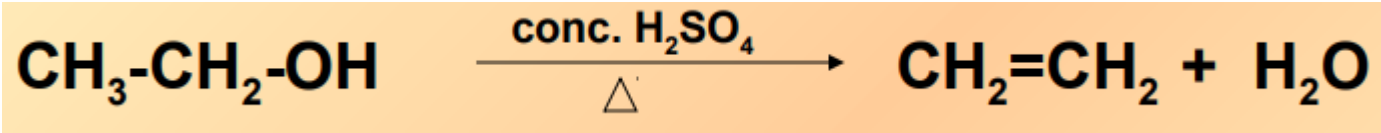
$$R\text{-}OH + H\text{-}X \rightarrow R\text{-}X + H_2O$$

$$R\text{-}OH + SOCl_2 \rightarrow R\text{-}Cl + SO_2 + HCl$$

REACTIONS OF ALCOHOLS

Dehydration





REACTIONS OF ALCOHOLS

Formation of ether (Williamson ether synthesis)

$$R\text{-}O^{\cdot} + R'\text{-}X \rightarrow R\text{-}O\text{-}R' + X^{\cdot}$$

alkoxide

(R' must be primary)

References

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