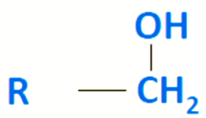
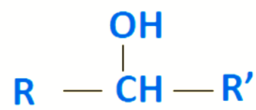
Ch(9): Alcohols
$C_nH_{2n+2}O$

I-Classes of alcohols

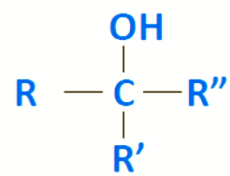
Alcohols are classified into three classes :



Primary ($R-CH_2-OH$)



Secondary ($R-CHR'-OH$)



Tertiary ($R-CR'R''-OH$)

R: is a hydrocarbon chain (CH_3- CH_2- …) and it may be linear or branched.

II-IUPAC names of alcohols

The names of alcohols are derived from the names of alkanes with addition of the suffix "ol" .

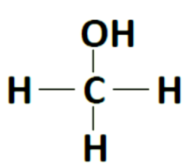
The name depends on the number of carbon in the main chain as the following :

1 C : methanol   2 C: ethanol   3C : propanol   4C : butanol

5C : pentanol   6C : hexanol   7C : heptanol   8C : octanol

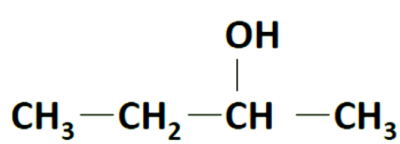
9C : nonanol   10 C: decanol

Examples (IUPAC names and classes)



Methanol

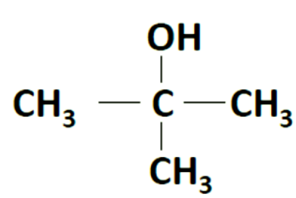
$CH_3-CH_2-CH_2-CH_2-OH$ 1-butanol



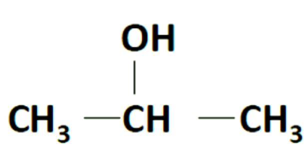
2-butanol

CH_3-CH_2-OH Ethanol

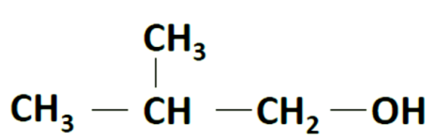
$CH_3-CH_2-CH_2-OH$ 1-propanol



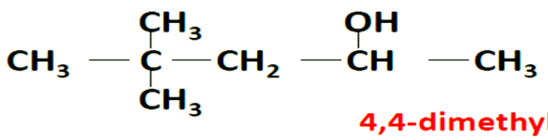
2-methyl-2-propanol



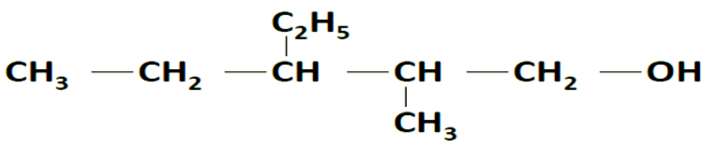
2-propanol



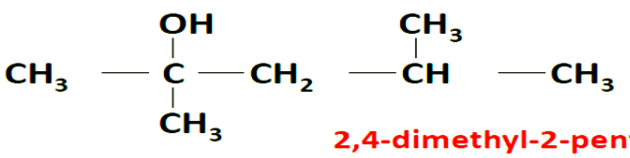
2-methyl-1-propanol



4,4-dimethyl-2-pentanol



3-ethyl-2-methyl-1-pentanol



2,4-dimethyl-2-pentanol

Note

The numbering of the main chain is from the side near to the (OH).
If the numbering is the same from the two sides , the correct numbering is from the side that holds more branches.

Names of branches

CH_3 - : methyl
$CH_3 - CH_2$ - : ethyl
C_2H_5 - : ethyl

III-Reactions of Alcohols

The reactivity of an alcohol depends on the nature of its class.

Alcohols can undergo many types of reactions.

The two main types of reactions of alcohols are :

- **Mild oxidation reactions.**
- **Esterification reactions.**

1. Mild oxidation reactions

The mild oxidation is the reaction that transforms the functional group (-OH) into other groups (carbonyl group :-C=O or carboxyl group: –COOH) without change neither in the number carbon, nor in the shape of hydrocarbon chain of the molecule.

The mild oxidation of alcohols can be carried out in three ways:

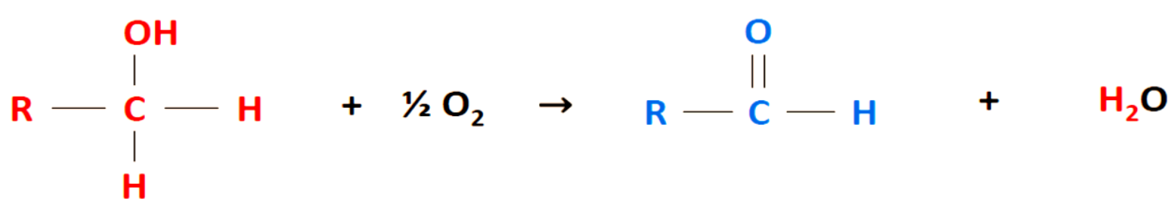
- **Catalytic oxidation in the presence of oxygen.**
- **Catalytic dehydrogenation in the absence of oxygen.**
- **Oxidation in the presence of strong oxidants such as MnO_4^- and $Cr_2O_7^{2-}$**

1.1. Catalytic oxidation in the presence of oxygen and Cu or Pt as catalyst

The mild oxidation of primary alcohol leads to the formation of aldehyde:

Primary alcohol + oxygen → Aldehyde + water

$C_nH_{2n+2}O + \frac{1}{2} O_2 \rightarrow C_nH_{2n}O + H_2O$



The continuous mild oxidation of primary alcohol in the presence of an excess of O_2 produces carboxylic acids :

Primary alcohol	+	oxygen	→	Carboxylic acid	+	water
$C_nH_{2n+2}O$	+	O_2	→	$C_nH_{2n}O_2$	+	H_2O

$$R - \underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}} - H \quad + \quad O_2 \quad \rightarrow \quad R - \overset{\displaystyle O}{\overset{\|}{C}} - OH \quad + \quad H_2O$$

The secondary alcohols can react <u>only with ½ O_2</u> and leads to the formation of ketones:

Secondary alcohol	+	Oxygen	→	Ketone	+	water
$C_nH_{2n+2}O$	+	½ O_2	→	$C_nH_{2n}O$	+	H_2O

$$R - \overset{\displaystyle OH}{\overset{|}{CH}} - R' \quad + \quad \tfrac{1}{2}\,O_2 \quad \rightarrow \quad R - \overset{\displaystyle O}{\overset{\|}{C}} - R' \quad + \quad H_2O$$

Tertiary alcohols cannot undergo any oxidation reaction:

Tertiary alcohol + ½ O_2(or O_2) → no reaction

The experimental conditions of the catalytic oxidation is :

1. presence of catalyst (Cu or Pt)
2. presence of oxygen.

<u>1.2. Catalytic dehydrogenation in presence of Cu or Pt as catalyst and the presence of heat and without oxygen.</u>

The dehydrogenation of primary alcohol leads to the formation of aldehyde:

Primary alcohol	→	Aldehyde	+	hydrogen gas
$C_nH_{2n+2}O$	→	$C_nH_{2n}O$	+	H_2

$$R - \underset{\displaystyle H}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}} - H \quad \xrightarrow{\text{Heat + Cu or Pt}} \quad R - \overset{\displaystyle O}{\overset{\|}{C}} - H \quad + \quad H_{2(g)}$$

The dehydrogenation of secondary alcohols leads to the formation of ketones:

Secondary alcohol	→	Ketone	+	hydrogen gas
$C_nH_{2n+2}O$	→	$C_nH_{2n}O$	+	H_2

$$R - \overset{\displaystyle OH}{\overset{|}{CH}} - R' \quad \xrightarrow{\text{Heat + Cu or Pt}} \quad R - \overset{\displaystyle O}{\overset{\|}{C}} - R' \quad + \quad H_{2(g)}$$

The tertiary alcohol cannot undergo dehydrogenation reaction.

The experimental conditions of dehydrogenation reaction are :

1. presence of catalyst (Cu or Pt)
2. presence of heat
3. Absence of oxygen

1.3. oxidation in presence of MnO_4^- or $Cr_2O_7^{2-}$

1.3.1. oxidation with MnO_4^-

Primary alcohol + MnO_4^- → Aldehyde + Mn^{2+}

$C_nH_{2n+2}O$ (Colorless) + MnO_4^- (Purple) → $C_nH_{2n}O$ (Colorless) + Mn^{2+} (slight pink)

Primary alcohol + excess of MnO_4^- → Carboxylic acid + Mn^{2+}

$C_nH_{2n+2}O$ (Colorless) + excess of MnO_4^- (Purple) → $C_nH_{2n}O_2$ (colorless) + Mn^{2+} (slight pink)

Secondary alcohol + MnO_4^- → Ketone + Mn^{2+}

$C_nH_{2n+2}O$ (Colorless) + MnO_4^- (Purple) → $C_nH_{2n}O$ (colorless) + Mn^{2+} (slight pink)

Secondary alcohols give only ketones if an excess of MnO_4^- is added.

The tertiary alcohols do not react neither with MnO_4^- nor with $Cr_2O_7^{2-}$

Note

The redox reactions with MnO_4^- need balance in acidic medium (adding H^+) by using the two half equations method.

Secondary alcohols gives only ketones if an excess of $Cr_2O_7^{2-}$ is added.

Secondary alcohol + $Cr_2O_7^{2-}$ → Ketone + Cr^{3+}

$C_nH_{2n+2}O$ (Colorless) + $Cr_2O_7^{2-}$ (orange) → $C_nH_{2n}O$ (colorless) + Cr^{3+} (green)

1.3.2. oxidation with $Cr_2O_7^{2-}$

Primary alcohol + $Cr_2O_7^{2-}$ → Aldehyde + Cr^{3+}

$C_nH_{2n+2}O$ (Colorless) + $Cr_2O_7^{2-}$ (orange) → $C_nH_{2n}O$ (Colorless) + Cr^{3+} (green)

Primary alcohol + excess of $Cr_2O_7^{2-}$ → Carboxylic acid + Cr^{3+}

$C_nH_{2n+2}O$ (Colorless) + excess of $Cr_2O_7^{2-}$ (orange) → $C_nH_{2n}O_2$ (colorless) + Cr^{3+} (green)

Note: the esterification reaction is explained in Ch(11) : carboxylic acids