Chapter 8: Alcohols

- **<u>Monoalcohol</u>**: is an organic compound consists of the elements (C,H&O) with general formula $C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$ and hydroxyl functional group (-OH)
  - General molecular formula : (R-OH)
- **<u>Classes of monoalcohol:</u>**

Alcohols
- 1^o alcohol (RCH_2OH): the C-atom that is attached to (OH) carries 2 H-atoms.
- 2^o alcohol (RR'CHOH): the C-atom that is attached to (OH) carries 1 H-atom.
- 3^oalcohol (RR'R''COH): the C-atom that is attached to (OH) carries no H-atoms.

- **<u>IUPAC Nomenclature:</u>**

Alkane → Alkanol

CH_3OH : methanol (1^0)

CH_3-CH_2OH : ethanol (1^o)

$CH_3-CH_2-CH_2OH$: 1-propanol (1^o)

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$: 2-propanol (2^o)

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$: 4-ethyl-5-methyl-2-hexanol (2^o)

C_6H_5OH: phenol

$C_6H_5-CH_2-OH$: phenyl methanol (benzyl alcohol)

*** <u>Isomers of alcohol:</u>** structural isomers (skeletal and positional)

e.g butanol (C_4H_9OH):

a. $CH_3-CH_2-CH_2-CH_2-OH$: 1-butanol (1^o)

b. $CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$: 2-butanol (2^o)

c. $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$: 2-methyl-1-propanol (1^o)

d. $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$: 2-methyl-2-propanol or tertiary butanol (3^o)

- Positional isomers: (a & b) , (c & d)
- Skeletal isomers: (a & d) , (b & d)

- **Ether:** is an organic compound consists of the elements(C,H&O) with the general formula $C_2H_{2n+2}O$ and the functional group -O- (ether group).

  - General molecular formula: (R-O-R')

-**Nominclature:** Alkyl(R) Alkyl(R') ether

e.g CH_3-O-CH_3 : dimethyl ether

C_2H_5-O-CH_3 : ethyl methyl ether

CH_3-O-CH-CH_3 : (methyl ethyl) methyl ether or methyl isopropyl ether
        |
      CH_3

CH_3-O-CH_2-CH-CH_3 : methyl (2-methyl propyl) ether
                |
              CH_3

- **Alcohol and ether admits functional isomers.**

***e.g.* Isomers of $C_4H_{10}O$:**

Alcohol	Ether
a. CH_3-CH_2-CH_2-CH_2OH	e. CH_3-CH_2-CH_2-O-CH_3
b. CH_3-CH_2-CH-CH_3 | OH	f. CH_3-CH_2 -O-CH_2-CH_3
c. CH_3-CH-CH_2-OH | CH_3	g. CH_3-CH-O-CH_3 | CH_3
OH | d. CH_3-C-CH_3 | CH_3	

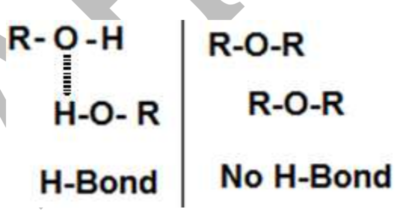
e.g. a & e are functional isomers.

- **Physical properties:**

Hydrogen bond: is the intermolecular force of attraction between H-atom of one molecule and the most electronegative element (F, O, N or Cl).

N.B: H with (F, N, O, or Cl) should be in the same functional group, bonded to each other.

- Alcohol has H-bond while ether does not.



- As no of C-atom or molar mass increases, Boiling point increases but solubility in water decreases. e.g CH_3OH (B.pt= 65 ^{0}C) , C_2H_5OH (B.pt= 78.5 ^{0}C)
- As no. of branches increases, boiling point decreases, but solubility increases.

e.g. CH_3-CH_2-CH_2-CH_2-OH (B.pt= 117 ^{0}C) , CH_3-CH-CH_2-OH (B.pt= 108 ^{0}C)
                                  |
                                CH_3

- The presence of H-bond increases the boiling point and the solubility in water..

  e.g. C_2H_5OH (B.pt = 78.5 ^{0}C) but CH_3-O-CH_3 (B.pt= -25^{0}C)

	Boiling point	Solubility in water
Molar mass(↑)	↑	↓
Branch(↑)	↓	↑
H-bond(↑)	↑	↑

- **<u>Chemical properties (Chemical Reactions)</u>:**

  - Common properties: Substitution and Esterification.

  - Different properties: Mild Oxidation.

1) <u>Substitution Reactions</u>:

a) $ROH + \underset{\text{Phosphorus Pentachloride}}{PCl_5} \rightarrow \underset{\text{Chloroalkane}}{RCl} + HCl + \underset{\text{phosphorous oxytrichloride}}{POCl_3}$

e.g $CH_3-CH_2-OH + PCl_5 \rightarrow CH_3-CH_2-Cl + HCl + POCl_3$

b) $ROH + \underset{\text{Thionyl chloride}}{SOCl_2} \rightarrow RCl + HCl + SO_2$

e.g. $CH_3-\underset{\underset{CH_3}{|}}{C}HOH + SOCl_2 \rightarrow CH_3-\underset{\underset{CH_3}{|}}{C}H-Cl + HCl + SO_2$

2) <u>Esterification Reaction</u>:

$$\text{Alcohol + Carboxylic acid} \underset{}{\overset{H2SO4/\ \Delta}{\rightleftharpoons}} \text{Ester + water}$$

* Forward rxn is esterification, while backward rxn is hydrolysis.

* Characteristics of the rxn: slow- reversible - athermic.

$$R'OH + \underset{\substack{\text{Carboxylic acid}\\ \text{(Alkanoic acid)}}}{RCOOH} \underset{\Delta}{\overset{H_2SO_4}{\rightleftharpoons}} \underset{\substack{\text{Ester}\\ \text{Alkyl(R') Alkanoate(R)}}}{RCOOR'} + H_2O$$

part from carboxylic acid — $\boxed{RCOO}\boxed{R'}$ — part from alcohol

e.g. $CH_3-\underset{\underset{CH_3}{|}}{C}H-OH + CH_3COOH \rightleftharpoons CH_3-COO-\underset{\underset{CH_3}{|}}{C}H-CH_3 + H_2O$

<u>Hydrolysis of ester:</u>

$RCOOR' + H_2O \rightleftharpoons R'OH + RCOOH$ (slow-reversible- athermic)

<u>Percent yield of esterification</u>:

$$\text{Alcohol} + \text{Carboxylic acid} \rightleftharpoons \text{Ester} + \text{water}$$

t_0:	$n(\text{alcohol})_0$	$n(\text{acid})_0$	0	0
$t_{eq.}$:	$n(\text{alcohol})_0 - x$	$n(\text{acid})_0 - x$	x	x

$$\%\ \text{yield} = \frac{n(actual)}{n(theoritical)} \times 100$$

$$= \frac{n(ester)teq}{n(ester)\max} \times 100$$

$$= \frac{x}{n(\lim iting)} \times 100$$

- % yield of esterification in case of equimoler : 1^0(67%) , 2^0 (60%), 3^0(1-5%)
- % yield of esterification in case of non-equimoler increases, since according to le chatelier's principle , the excess amount of the reagent shifts the rxn forward toward forming more actual amount.

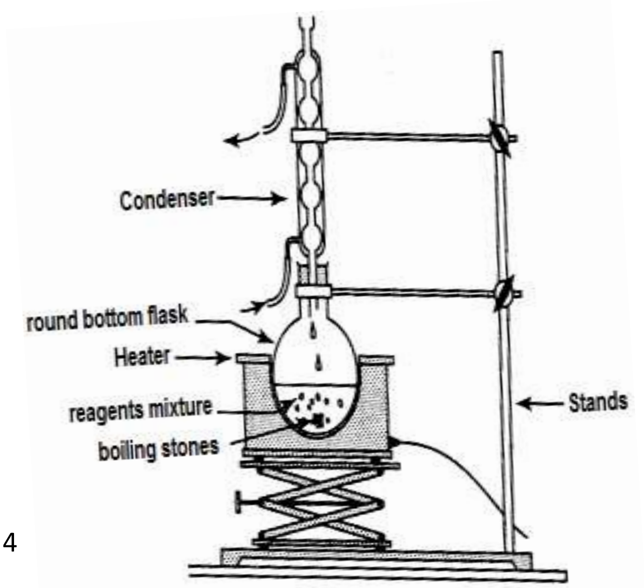
<u>Notes:</u>

- ***Heating the mixture doesn't affect the % yield of the rxn at equilibrium , because it is athermic.***
- ***To increase the rate of esterification: 1. Increase T 2. Use catalyst 3. Increase the concentration of reactants.***
- ***To increase the yield of esterification:***
  1. ***Remove water molecules from the rxn medium by using a dehydrating agent (e.g sulfuric acid)***
  2. ***Increase the amount of the excess reagent.***

Note : Replacing carboxylic acid by their derivatives acid anhydride or acylchloride gives higher yield since the reaction becomes complete.

<u>Role of:</u>

- ***<u>H_2SO_4:</u>***
- ***In small amount: is a catalyst increases the rate of the reaction.***
- ***In high concentrated amount: in addition to catalyst, it is a dehydrating agent, eliminates water from the rxn $\Rightarrow$ the rxn displaces forward $\Rightarrow$ n(ester)$_{actual}$ increases = > yield increases.***



Reflux Apparatus

- ***Heating**: to increase the rate of the rxn, since T is akinetic factor.*

- ***Reflux heating**: To extend the time of heating to increase the rate of esterification without losing any of the reaction components by condensinng their vapors and get them back to the reaction medium..*
- ***Anti-bombing stones**: regulate boiling by decreasing the inside pressure to avoid the bombing of the apparatus.*

3) Mild Oxidation:

*Mild oxidation: is an oxidation process takes place without breaking down the C-Chain.

Ways of mild oxidation:

A. Catalytic oxidation (+ O_2 /Cu)
B. Catalytic Dehydrogenation (-H_2/ Cu + heat)
C. Oxidation by oxidizing agent ($KMnO_4$, $K_2Cr_2O_7$, ….)

Note: Mild oxidation allows identifying the class of an alcohol.

Class of alcohol	Product of mild oxidation	Continuous mild oxidation
1^0	Aldehyde	Carboxylic acid
2^0	Ketone	non
3^0	non	non

A) Catalytic oxidation:

For 1^0alcohol:

$$\underset{1^o\text{ alcohol}}{RCH_2OH} + \underset{\text{limitig}}{\frac{1}{2}O_2} \xrightarrow[-H2O]{Cu} \underset{\substack{\text{Aldehyde}\\ \text{(alkanal)}}}{R-\overset{\overset{O}{\|}}{C}-H} + \underset{\text{excess}}{\frac{1}{2}O_2} \longrightarrow \underset{\substack{\text{carboxylic acid}\\ \text{(alkanoic acid)}}}{R-\overset{\overset{O}{\|}}{C}-OH}$$

e.g. step 1: $CH_3\text{-}CH_2\text{-}OH + \underset{\text{limiting}}{\frac{1}{2}O_2} \xrightarrow{Cu} \underset{\text{ethanal}}{CH_3-\overset{\overset{O}{\|}}{C}-H} + H_2O$

step 2: $CH_3-\overset{\overset{O}{\|}}{C}-H + \frac{1}{2}O_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH$ (Continuous mild oxidation)

……

over all : $CH_3\text{-}CH_2\text{-}OH + \underset{\text{Excess}}{O_2} \longrightarrow \underset{\text{ethanoic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + H_2O$

<u>For 2^0alcohol:</u>

$$RR'CHOH + \frac{1}{2}O_2 \xrightarrow{Cu} R-\overset{\overset{O}{||}}{C}-R' + H_2O$$

2^0 alcohol — ketone (Alkanone)

$$\text{e.g } CH_3\text{-}CH(CH_3)\text{-}OH + \frac{1}{2}O_2 \xrightarrow{Cu} CH_3\text{-}\overset{\overset{O}{||}}{C}\text{-}CH_3 + H_2O$$

propanone

<u>For 3^0alcohol:</u>

$$RR'R''C\text{-}OH + \frac{1}{2}O_2 \longrightarrow \text{no rxn}$$

B) <u>Catalytic Dehydrogenation</u>:

<u>For 1^0 alcohol:</u>

$$RH_2OH \xrightarrow[300^oC]{Cu} R-\overset{\overset{O}{||}}{C}-H + H_2$$

1^o alcohol — Aldehyde

$$\text{e.g } CH_3CH_2OH \xrightarrow[300^oC]{Cu} CH_3-\overset{\overset{O}{||}}{C}-H + H_2$$

<u>For 2^0alcohol:</u>

$$RR'CH\text{-}OH \xrightarrow[300^oC]{Cu} R\text{-}\overset{\overset{O}{||}}{C}\text{-}R' + H_2$$

2^o alcohol — Ketone

$$\text{e.g } CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}OH \xrightarrow[300^oC]{Cu} CH_3\text{-}\overset{\overset{O}{||}}{C}\text{-}CH_3 + H_2$$

<u>For 3^0alcohol:</u>

$$RR'R''C\text{-}OH \xrightarrow[300^oC]{Cu} \text{no rxn}$$

C) <u>Oxidation by oxidant</u>: $(Cr_2O_7^{2-}/Cr^{3+})$ & (MnO_4^{-}/Mn^{2+})

$$\underset{\text{Limiting}}{RCH_2OH + \text{oxidant}} \longrightarrow \underset{\text{excess}}{RCHO + \text{Oxidant}} \longrightarrow RCOOH$$

<u>For 1^0alcohol:</u>

$$\underset{1^o\text{ alcohol}}{RCH_2OH} + \underset{\text{limiting}}{Cr_2O_7^{2-}} \longrightarrow \underset{\text{aldehyde}}{RCHO} + Cr^{3+}$$

Balanced: $3RCH_2OH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3\,RCHO + 2\,Cr^{3+} + 7\,H_2O$

(Limiting amount) (aldehyde)

e.g $3\,CH_3CH_2OH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3\,CH_3CHO + 2\,Cr^{3+} + 7\,H_2O$

Balanced: $3\,RCH_2OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 3\,RCOOH + 4\,Cr^{3+} + 11\,H_2O$ (continuous mild oxidation)

1° alcohol (Excess amount) carboxylic acid

e.g $3\,CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \longrightarrow 3\,CH_3COOH + 4\,Cr^{3+} + 11H_2O$

For 2⁰alcohol:

$RR'CHOH + Cr_2O_7^{2-} \longrightarrow RCOR' + Cr^{3+}$

2° alcohol ketone

Balanced: $3RR'CHOH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3\,RCOR' + 2\,Cr^{3+} + 7H_2O$

e.g $3\,CH_3CH(CH_3)OH + Cr_2O_7^{2-} + 8H^+ \longrightarrow 3\,CH_3COCH_3 + 2\,Cr^{3+} + 7H_2O$

For 3⁰alcohol:

$RR'R''C\text{-}OH + Cr_2O_7^{2-} \longrightarrow$ no rxn

Note:

- Esterification needs an experimental reflux heating since alcohol is volatile.
- All mild oxidation needs experimental distillation to get the aldyhyde or the ketone formed since they are volatile compounds.
- Continues mild oxidation needs an experimental reflux heating since the aldehyde formed from the first mild oxidation is volatile.

  * Volatile : has low boiling point