$ksp = \left(\frac{[P]}{[R]}\right)$

UNIT-6 Some Important Oxygen-Containing Organic Compounds

Introduction: The oxygenated hydrocarbons (oxygen-containing organic cpds) are organic cpds that contain oxygen in their functional groups. They include alcohols, ethers, aldehydes, ketones, carboxylic acids and esters.

Alcohols and Ethers:

- Alcohols and ethers are functional isomers, i.e they have the same molecular formula but d/t in their functional group.

$R-CH_2-OH$	$R-O-R$	Where R & R' are the same or d/t alkyl or aryl group.
Alcohols	Ether	
E.g $CH_3-CH_2-CH_2-OH$	$CH_3-CH_2-O-CH_3$	
MF = C_3H_8O	C_3H_8O	
alcohol	ether.	

Alcohols

- Alcohols are oxygenated-derivatives of hydrocarbons in w/h one or more of the hydrogen atom(s) in the hydrocarbon have been replaced by a hydroxyl (-OH) group.
- The functional group of alcohol is an -OH (hydroxyl group), which is responsible for imparting certain chemical and/or physical properties to the compound. The hydroxyl group is directly attached to carbon atom(s) of an aliphatic system.

E.g $CH_3-CH_2-CH_2-OH$ 1-propanol (propan-1-ol)

Classification of Alcohols

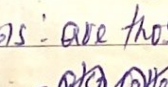
- Depending on the number of -OH group an alcohol contain, alcohols can be classified into:

1) Monohydric Alcohols: are those containing only one -OH group per a molecule.
   - They have a general molecular formula of $C_nH_{2n+1}OH$

   Eg. CH_3-CH_2-OH (ethanol).

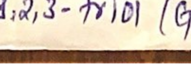
ii- Dihydric alcohols: are those containing two -OH groups per a molecule.
   - They have a general formula of $C_nH_{2n}2OH$.

   Eg.



$H_2\underset{OH}{C}-\underset{OH}{CH_2}$ Ethane-1,2-diol (Ethylene glycol)

iii- Trihydric alcohols: are those containing three -OH groups per a molecule.
   - ~~also called~~ Eg:



$H_2\underset{OH}{C}-\underset{OH}{CH}-\underset{OH}{CH_2}$

Propane-1,2,3-triol (Glycerine or glycerol)

316193

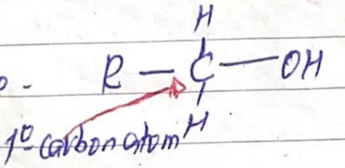
IV- Polyhydric alcohols: are those containing three or more -OH groups per a molecule in their structure.

Classification of Monohydric Alcohols

- Monohydric alcohols may be furtherly classified according to the carbon atom (1°-carbon, 2°, 3°-) to which the hydroxyl group is attached.

i- Primary alcohols: are those in which the hydroxyl group is attached to the primary (1°-) carbon atom (the carbon atom attached to only one alkyl group).

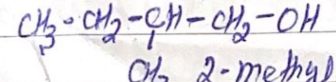
General structure -



$R-CH_2-OH$

primary alcohol.

E.g

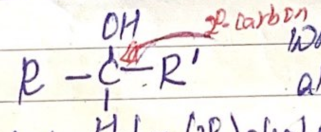


$CH_3-CH_2-CH(CH_3)-CH_2-OH$

2-methyl-1-butanol.

ii- Secondary (2°) alcohols: ~~are~~ are those in which the -OH group is attached to the secondary (2°-) carbon atom (the carbon atom directly attached to two alkyl groups.

General structure -

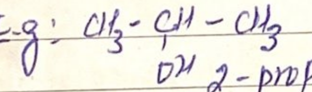


$R-CH(OH)-R'$

Where R & R' may be the same or d/t alkyl or aryl groups.

secondary (2°) alcohol.

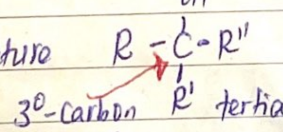
E.g:



$CH_3-CH(OH)-CH_3$

2-propanol.

iii- Tertiary (3°) alcohols: are those in which the -OH group is attached to the tertiary (3°) carbon atom (the carbon atom directly attached to three alkyl groups.



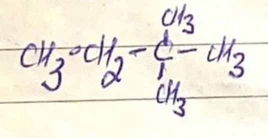
$R-C(OH)(R')-R''$

G. structure

Where R, R' and R'' are the same or d/t.

tertiary (3°) alcohol

E.g



$CH_3-CH_2-C(CH_3)_2-CH_3$

2-methyl-2-butanol.

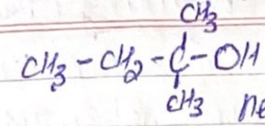
Nomenclature of Alcohols

i- Common name: The common name of an alcohol is derived from the common name of the alkyl group and adding the word alcohol to it.

E.g: $CH_3-CH_2-CH_2-OH$

propyl alcohol.

Eg-2:



$$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

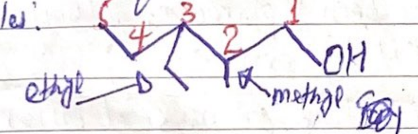
neopentyl alcohol.

ii- IUPAC Name: Rules for IUPAC naming

1- Select the longest continuouse chain that contain the -OH group.
2- Numbering starting from the one end closest to the OH group
3- The positions of the -OH group and other substituents are indicated by using the numbers of carbon atoms to which these are attached.
4- For monohydric alcohols change the name of the alkane corresponding to the chain by dropping the final "e" and adding the suffix -ol.
5- For naming of polyhydric alcohol (2-OH or more) the "e" of alkane is retained and the ending "ol" is added. ~~The~~
6- The number of OH groups and the same side chains are indicated by adding the multiplicative prefix, di, tri.... before ol and the name of side chains.
The name of side chains arranged aliphabetically.

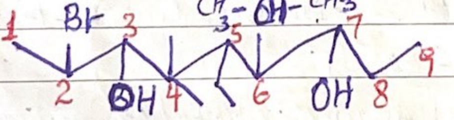
Examples:

1)



IUPAC name: 3-ethyl-2-methyl pentan-1-ol OR
3-ethyl-2-methyl-1-pentanol.

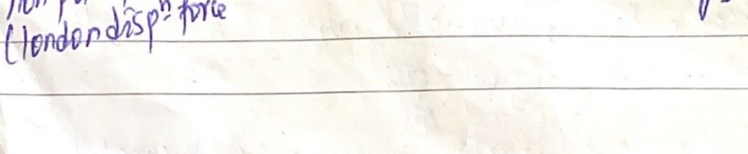
2)



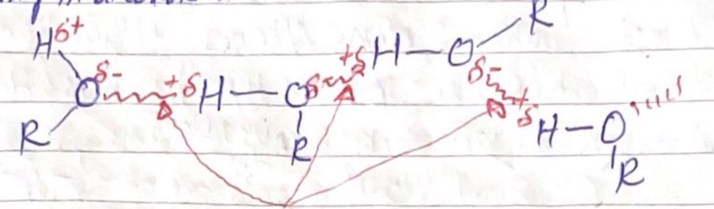
IUPAC Name: 2-bromo-5-ethyl-6-isopropyl-4-4-dimethyl-3,7-nonanediol (OR)
2-bromo-5-ethyl-6-isopropyl-4,4-dimethylnonane-3,7-diol.

Physical properties of Alcohols.

- The intermolecular force of interactions (both london dispersion force and H-bonding) are responsible for the physical properties of alcohols

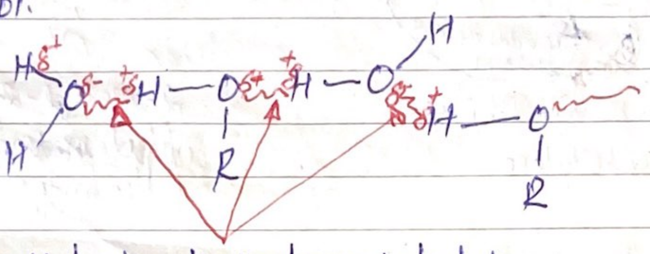


- The hydroxyl group (-OH) in an alcohol is polar, as a result, there is a significant H-bonding in alcohols.



Hydrogen bonding b/n alcohol molecules.

- lower members of alcohols are highly polar liquids. As a result, they are completely soluble in polar substance (like H_2O). This is due to the formation of H-bonding b/n water molecule and an alcohol.



H-bonding b/n water and alcohol.

- As the molecular size (mass), the non-polar portion of an alcohol increases, the polarity of an alcohol decreases due the strengthen of london disp^{n} force, and thus the solubility with water also decreases.
- Branched-chain isomers of alcohols are easily soluble than straigh chain alcohols. This is due to the fact that the molecules become spherical in shape that reduces the surface area in contanct b/n molecules which results the weaker london disp^{n} force b/n them and the stronger H-bonding will expriance that makes them more soluble.
- polyhydric alcohols are more soluble than monohydric alcohols, b/ce of the more number of -OH groups form more H-bonding with water.

i.e solubility of polyhydric > dihydric > monohydric.

Solubility of 3^{o}-alcohol > 2^{o}-alcohol > 1^{o} alcohols.

- Due to the H-bonding in alcohols, they have higher melting and boiling points than hydrocarbons of comparable molecular size (mass).
- As the molecular size increase, the more stronger in london disp^{n} force, and the more the number of -OH groups, the more number of H-bonding b/n them w/h both results the higher melting and boiling points.
- Branched chain isomers have lower melting and boiling points than straight chain alcohols, due to the weaker london disp^{n} force in branched-chain alcohols.

Note: 1^{o}alcohol > 2^{o}alcohol > 3^{o}alcohol. Table 6.1 page 273

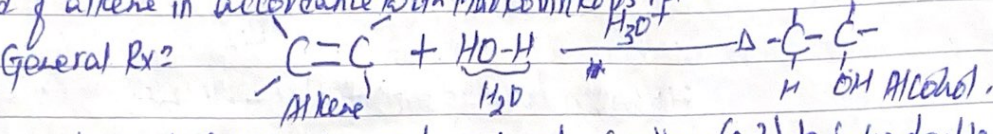
Preparation of Alcohols.

- The general laboratory methods of prepn of alcohols are:

A - Acid catalyzed hydration of Alkenes (Hydration of alkenes)

- In the presence of diluted acids (such as H_2SO_4, or H_3PO_4), Water is added to the double bond of alkene in accordance with Markovinkov's rule.

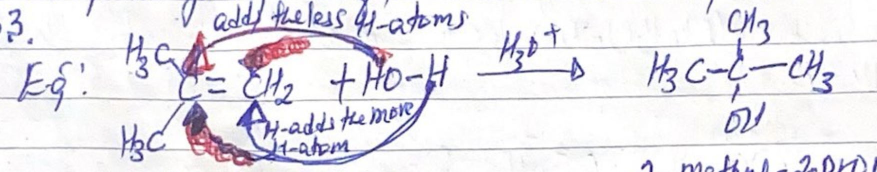
General Rx:



$$\underbrace{>C=C<}_{\text{Alkene}} + \underbrace{HO{-}H}_{H_2O} \xrightarrow{H_3O^+} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- \text{ Alcohol.}$$

- The rx changes the hybridization of the carbon atom in alkene (sp^2) in the double bond to sp^3.

E.g:



$$(H_3C)_2C{=}CH_2 + HO{-}H \xrightarrow{H_3O^+} H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3$$

2-methyl propene
Isobutylene.

2-methyl-2-propanol.
(tert-butyl alcohol (or
(Neobutyl alcohol.)

B - Hydrolysis of alkyl halides

- Warming alkylhalides with NaOH forms alcohols.

General rxn: $\underset{1^\circ\text{ alkyl halide}}{R-CH_2-X(Cl,Br,I)} + NaOH \xrightarrow{heat} \underset{1^\circ\text{ alcohol}}{R-CH_2-OH} + NaX$

E.g:- $\underset{\text{propyl bromide}}{CH_3-CH_2-CH_2-Br} + NaOH \xrightarrow{heat} \underset{\text{1-propanol}}{CH_3-CH_2-CH_2-OH} + NaBr$

(1°-alkyl halides gives good yield of 1°-alcohols).

ws 2°-alkyl halides gives mixture of alcohol and alkene.

E.g2 $CH_3-\underset{Br}{CH}-CH_3 + NaOH \xrightarrow{heat} \underset{\text{1-propene}}{CH_2=CH-CH_3} + \underset{\text{2-propanol}}{CH_3-\underset{OH}{CH}-CH_3} + NaBr + H_2$

C - Hydrolysis of Esters.

- Heating esters with KOH produces alcohols:

General rx: $\underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + KOH \xrightarrow{heat} R-COOK + \underset{\text{alcohol}}{R'OH}$

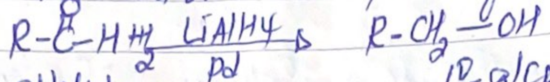
E.g: $\underset{\text{ethyl acetate}}{CH_3-COOCH_2-CH_3} + KOH \xrightarrow{heat} CH_3COOK + \underset{\text{ethanol}}{CH_3CH_2OH}$

Note, Methods B and C involve the replacement of other groups by the -OH group. Hence they are substitution rxns.

D- By Reduction of Carbonyl compounds (Aldehydes & ketones)

→ Aldehyde under reduction rx^n in the presence of $LiAlH_4$ (R. agent) yields 1°-alcohol

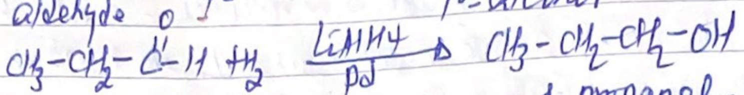
G. rx^n:



$R-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow[Pd]{LiAlH_4} R-CH_2-OH$

aldehyde 1°-alcohol.

Eg:

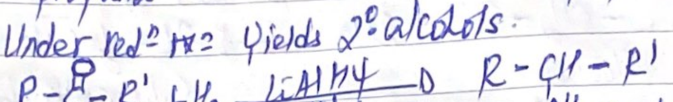


$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow[Pd]{LiAlH_4} CH_3-CH_2-CH_2-OH$

propanal 1-propanol.

→ Ketones under red^n rx^n yields 2° alcohols.

G. rx^n:

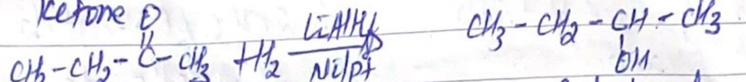


$R-\overset{O}{\overset{\|}{C}}-R' + H_2 \xrightarrow[Ni/Pt]{LiAlH_4} R-\underset{OH}{\underset{|}{CH}}-R'$

RCOR' 2°-alcohol.

ketone

Eg:



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + H_2 \xrightarrow[Ni/Pt]{LiAlH_4} CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-CH_3$

2-butanone 2-butanol.

Ethanol (Ethyl alcohol)

(Take a short-note from your text from page 275-276 please!)

Chemical properties of Alcohols.

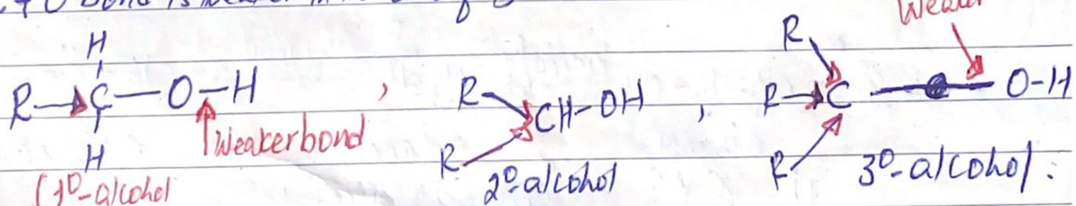
→ Reactions of alcohols may involve the cleavage of the oxygen-hydrogen bond (R-O⦙H) or the carbon oxygen bond (R⦙OH), i.e the chxs rx^n of alcohol are in it's functional group of the -OH group.

I- Rx^{n}s of alcohol involving cleavage of -O⦙H bond (Rx^n as an acid).

~~[illegible] with active metals ([illegible] Ca)~~

~~Alcohols react with active metal~~

→ The O-H bond is weaker in primary alcohols as electron density increases between O-H bond and the hydrogen tends to separate as a proton (H^+), while C⦙O bond is weaker in the case of 3°-alcohols.



→ Thus 1°-alcohols give the most of rx^n by cleavage of O-H bond while 3° alcohols are most reactive b/ce of the cleavage of C⦙O bond.

→ Hence O-H bond cleavage reactivity order:

1°-alcohol > 2°-alcohol > 3°-alcohol.

- Alcohols have ~~a~~ acidic nature but are not acidic enough to react with alkaline KOH or NaOH.
- Their acidic nature decreases with increasing of an alkyl groups on -OH bonded carbon atom. ~~i.e~~

Acidic order : 1° alcohol > 2° alcohol > 3° alcohol.

A- Reaction with active metals (such as Li, Na, K, Mg, Ca ---)

- Alcohols react with active metals to librate H_2 gas and to form metal alkoxide.

G.rx^n: $2R-CH_2-OH + 2Na \longrightarrow 2R-CH_2-\overset{-}{O}\overset{+}{Na} + H_2$

1 Alcohol — Sodium alkoxide.

- Alcohol act as a Bronsted-lowery acid

E.g. $2CH_3-CH_2-OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2$

Ethanol — Sodium ethoxide.

B- Oxidation of Alcohols.

- Its oxidation rx^n product depend on the type of alcohol and the nature of oxidizing agents.

i- Oxidation of 1° alcohols.

1) Using mild-oxidizing agents

- 1° alcohols yield aldehydes.

$R-CH_2-OH \xrightarrow{Cu} R-CHO \ (R-\overset{O}{\overset{\|}{C}}-H$

E.g. $CH_3-CH_2-CH_2-OH \xrightarrow{Cu} CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$

1-propanol — propanal

2) Using strong oxidizing agents (such as acidified $KMnO_4$ or $K_2Cr_2O_7$ or CrO_3 in H_2SO_4)

$1°\text{-alcohol} \xrightarrow{[O]} R-CHO \xrightarrow{[O]} R-COOH$

i.e $R-CH_2-OH \xrightarrow[{[O]}]{KMnO_4/H^+} R-\overset{O}{\overset{\|}{C}}-H \xrightarrow[{[O]}]{KMnO_4/H^+} R-\overset{O}{\overset{\|}{C}}-OH$

1° alcohol — aldehyde — C. Acid.

E.g. $CH_3-CH_2-OH \xrightarrow{KMnO_4/H^+} CH_3\overset{O}{\overset{\|}{C}}H \xrightarrow{KMnO_4} CH_3-\overset{O}{\overset{\|}{C}}-OH$

ethanol — ethanal — ethanoic acid.

ii- Ox^n of Secondary Alcohols

- Yields ketones.

G.rx^n: $R-\underset{OH}{\underset{|}{C}}H-R' \xrightarrow{[O]\text{-O-agent}} R-\overset{O}{\overset{\|}{C}}-R'$

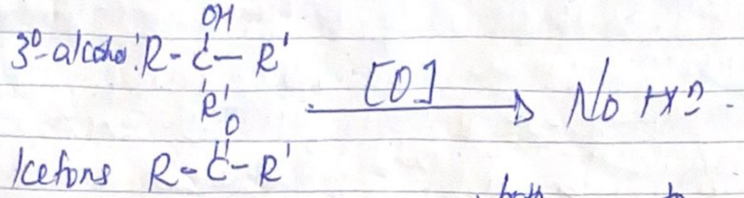
2° alcohol — ketone

E.g = $H_3C-CH_2-\underset{CH_3}{\underset{|}{C}}H-OH \xrightarrow{KMnO_4/H^+} H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

2-methyl butanol — 2-butanone.

page - 8 -

iii- Under normal conditions 3° alcohols & ketones are generally resistant to ox^n.



3°-alcohol: $R-\overset{OH}{\underset{R'}{C}}-R' \xrightarrow{[O]}$ No rxn.

ketons $R-\overset{O}{\overset{\|}{C}}-R'$

→ Under drastic conditions (High T°) both oxidizes to a mixture of two carboxylic acids.

C) Reaction ~~tw~~ with Carboxylic Acid (Esterification rxn).

- It ~~forms~~ yields ester and H_2O

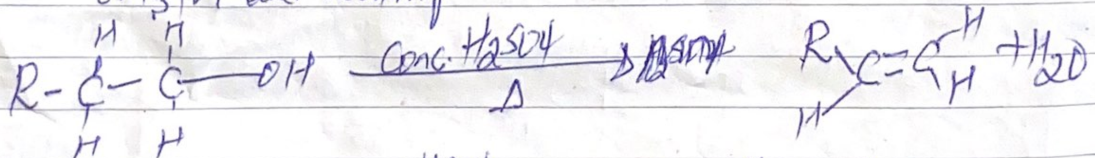
G-rxn: $\underbrace{R-CO\text{-}OH}_{C \cdot Acid} + H\text{-}O-R' \underset{}{\overset{Conc. H_2SO_4}{\rightleftharpoons}} \underset{Ester.}{R-COOR'} + H_2O$

E-g: $\underset{propanoic\ acid}{CH_3-CH_2COOH} + \underset{ethanol.}{HO-CH_2-CH_3} \overset{Conc. H_2SO_4}{\rightleftharpoons} \underset{ethyl\ propanoate}{CH_3CH_2COOCH_2CH_3} + H_2$

2- Reactions of alcohol involving cleavage of C—O bond (rxns as a base)

A- Dehydration of Alcohols (Removal of H_2O)

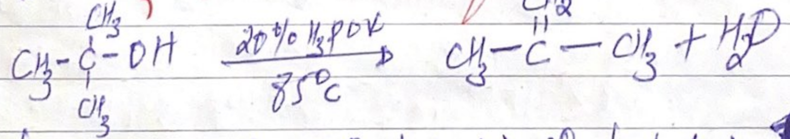
- It forms alkene on treating with an acid such as Conc. H_2SO_4 or H_3PO_4 and heating



$$R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-OH \xrightarrow[\Delta]{Conc. H_2SO_4} \overset{R}{\underset{H}{>}}C=C\overset{H}{\underset{H}{<}} + H_2O$$

E-g. $\underset{Ethanol}{CH_3-CH_2-OH} \xrightarrow[heat (170°C)]{Conc. H_2SO_4} \underset{ethene}{CH_2=CH_2} + H_2O \rightarrow$

Note: 1°- alcohols requires Conc acid and high T°.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[85°C]{20\% H_3PO_4} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH_3 + H_2O$$

Degree of dehydration order: 3°-alcohol > 2° alcohol > 1°-alcohol

B- Reaction of alcohols with hydrogen halides (HX).

- It forms alkyl halides.

G-rxn: $\underset{1°\ alcohol}{R-CH_2-OH} + HX \longrightarrow \underset{(X = I, Br, Cl)}{R-CH_2-X} + \underset{alkyl\ halides.}{H_2O}$

E-g: $\underset{1-propanol}{CH_3-CH_2-CH_2-OH} + HBr \longrightarrow \underset{n-propyl\ bromide.}{CH_3-CH_2-CH_2-Br} + H_2O$