17th July Wednesday

*Chapter: 2

classmate Date Page 49

Alcohol, Phenol & Ethers

ALCOHOL

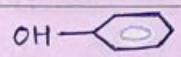
alcohol [-OH] [Hydroxy group]

* Classification:

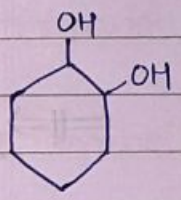
Based on 'OH'

I.) Monohydric alcohol: $R-CH_2OH$, CH_3OH, C_2H_5OH,

$CH_2=CH-OH$, $CH_2=CH-CH_2-OH$.



II.) Dihydric alcohol: $CH_2(OH)-CH_2(OH)$, $CH_2(OH)-CH_2-CH_2(OH)$,



ethylene glycol

III.) Trihydric alcohol: $CH_2(OH)-CH(OH)-CH_2(OH)$ glycerol

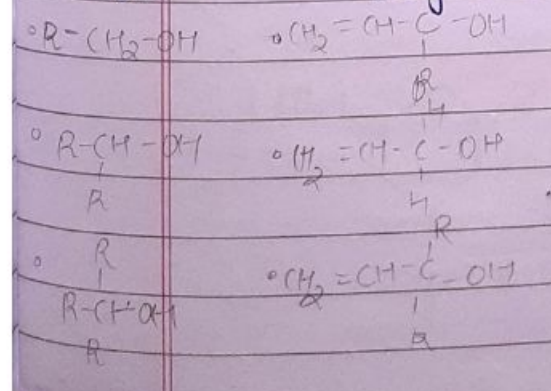
** Classification of monohydric alcohol:

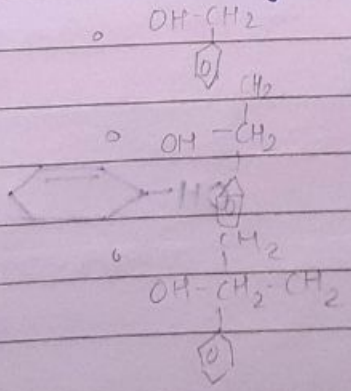
Alcohol containing sp^3 "C-OH bond"

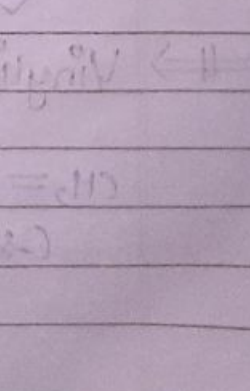
- Alkanol
  - → 1° alcohol
  - → 2° alcohol
  - → 3° alcohol
- Allylic Alcohol.
  - → 1° allylic alc.
  - → 2° allylic alc.
  - → 3° allylic alc.
- Benzylic alcohol
  - → 1° benzylic alc.
  - → 2° benzylic alc.
  - → 3° benzylic alc.

Alcohol containing sp^2 "C-OH bond".

- Vinylic alcohol
- Aryl alcohol





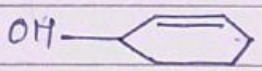


⇒ Classification of Alkanol:

1° Alkanol	2° Alkanol	3° Alkanol
• $R-CH_2-OH$	• $R-\underset{\displaystyle R}{\overset{\displaystyle |}{CH}}-OH$	• $R-\underset{\displaystyle R}{\overset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-OH$
eg: CH_3CH_2OH	$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-OH$	$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$
	isopropyl alcohol (IPA)	

⇒ Classification of Allylic alcohol:

1° Allylic alc.	2° Allylic alc.	3° Allylic alc.
$CH_2=CH-CH_2-OH$	$CH_2=CH-\underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}}-OH$	$CH_2=CH-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$



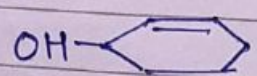
⇒ Classification of Benzylic alcohol:

1° Benzylic alc. | 2° Benzylic alc. | 3° Benzylic alc.

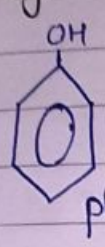
sp^3

⇒ Vinylic alcohol:

$CH_2=CH-OH$
$(-sp^2)$



⇒ Aryl alcohol:

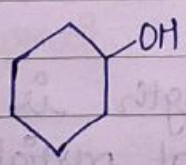


phenol

p-cresol.

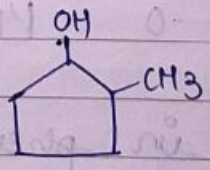
*	Compound	Common name	IUPAC
1.)	CH_3-OH	Methyl alcohol	Methanol.
2.)	$CH_3-CH_2-CH_2-OH$	n-propyl alcohol	1-Propanol.
3.)	$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$	Isopropyl alcohol	2-Propanol.
4.)	$CH_3-CH_2-CH_2-CH_2-OH$	n-Butyl alcohol	1-Butanol.
5.)	$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$	Sec-Butyl alcohol	2-Butanol.
6.)	$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-OH$	Isobutyl alcohol	2 Methyl-1-propanol.
7.)	$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$	Tert butyl alcohol	2-Methyl-2-propanol.
8.)	$HO-CH_2-H_2C-OH$.	Ethylene glycol	ethane-1,2-diol
9.)	$\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH_2}$	Glycerol	Propan-1,2,3-triol

(10.)



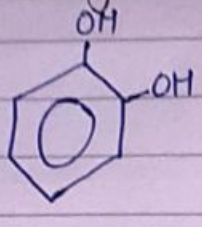
cyclohexanol

(11.)

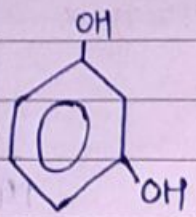


2-methyl pentanol.

* Dihydroxy derivatives of benzene:

1.) 

"Catechol"
[1,2-Benzenediol]

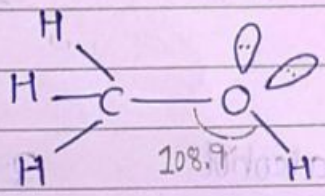
2.) 

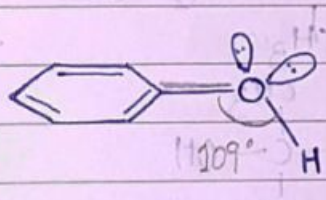
"Resorcinol"
[1,3-Benzenediol]

3.) 

"Quinol" [Hydroxyquinone]
[1,4-Benzenediol]

* Structure of Alcohol and Phenol:





$\Rightarrow$ C—O—H (108.9°)

Bond angle: 108.9°
[bcz of LP-LP repulsion
(more in compare to phenol)]

C—O—H (109°)

109°
[less effective LP repulsion
(bcz of bulky phenyl group)]

Bond l: C—O : 142 pm

C—O 135 pm.

* in phenol C—O bond length is shorter than alcohol bcz of partial double bond character's presence.

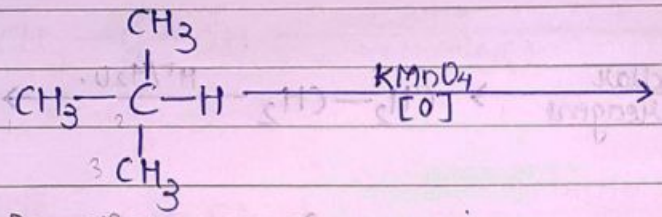
combustion ⟶ ⊕ of air ⊕ burned
oxidation ⟶ ⊕ of catalyst ⊕

* Preparation of Alcohol:

1.) From Alkane:

- $CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow[-KCl]{KOH\,(aq)} CH_3OH$.

methane — chloromethane — methanol.

- 

2-methyl propane — 2-methyl 2-propanol.

2.) From Alkene:

(A.) Acid Catalytic Hydration:

- $CH_2=CH_2 + H_2O \xrightarrow[\text{dil. } H_2SO_4]{H^+ \text{ or}} CH_3-CH_2-OH$.

ethene — ethanol.

- $CH_3-CH=CH_2 + H_2O \xrightarrow[\text{(MA) (carbocation)}]{H^+ \text{ or } H_2SO_4} CH_3-\underset{OH}{CH}-CH_3$

1-propene — 2-Propanol

(B.) Hydroboration-Oxidation Rxn:

- $CH_3-CH=CH_2 + H_2O \xrightarrow[II)\ H_2O_2/OH^-]{I)\ B_2H_6/THF} CH_3-CH_2-CH_2-OH$

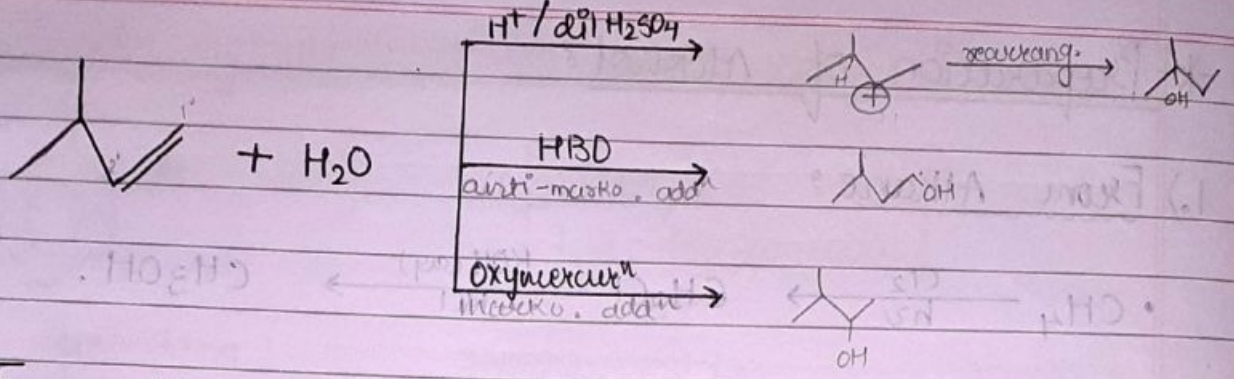
1-Propene — water — Anti-Markovnikov — Propanol.

(C.) Oxymercuration - Demercuration Rxn:

- $CH_3-CH=CH_2 + H_2O \xrightarrow[II)\ NaBH_4]{I)\ (CH_3COO)_2Hg} CH_3-\underset{OH}{CH}-CH_3$

1-Propene — water — (MA) (No carbocation) (acts as intermediate) — (Anti-addition) — 2-Propanol

Q:1.



3.) From Alkyne:

- $CH \equiv CH + 2H \xrightarrow[\text{reagent}]{\text{Lindlar}} CH_2 = CH_2 \xrightarrow{H^+/H_2O.} CH_3CH_2OH$

acetylene — etene — etanol

Q:2 $CH \equiv CH \longrightarrow$ Butanol.

$\Longrightarrow CH \equiv CH \xrightarrow{H_2/Pt} CH_3-CH_3 \xrightarrow{Nitz} CH_3CH_2CH_2CH_3 \xrightarrow[h\nu]{Cl_2} CH_3CH_2CH_2CH_2Cl$

$C_4H_{10}OH \xleftarrow{KOH}$

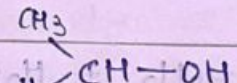
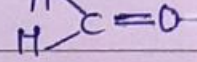
4.) From Alkyl Halide:

- $CH_3Cl \xrightarrow[(NSR)]{aq.\ KOH} CH_3OH + HCl$

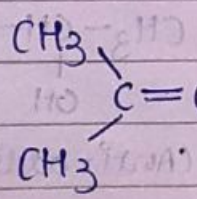
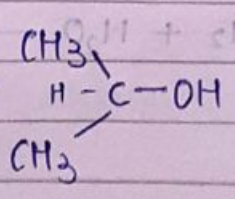
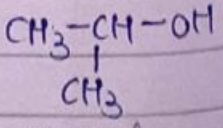
chloromethane — methanol — hydrochloric acid

- $CH_3CH_2Cl \xrightarrow[(NSR)]{aq.\ KOH} CH_3CH_2OH + HCl$

5.) From Carbonyl group reduction:

- acetaldehyde $\xrightarrow{LiAlH_4 / NiPt_4 / NaBH_4}$ 
-  $\xrightarrow{LiAlH_4 / NiPt_4 / NaBH_4} CH_3-OH$

formaldehyde — methanol

-  $\xrightarrow{LiAlH_4 / NiPt_4 / NaBH_4}$  or 

isopropyl alcohol

Q:3 $C_2H_6 \longrightarrow CH_4$

$\Rightarrow C_2H_6 \xrightarrow[h\nu]{Cl_2} C_2H_5Cl \xrightarrow{aq.KOH} C_2H_5OH \xrightarrow[KMnO_4]{[O]} CH_3COOH$

$CH_4 \xleftarrow{NaOH/CaO} CH_3COONa \xleftarrow{Na}$ (CH3COOH)

6.) Reduction of Acids and their derivatives:

- $CH_3-\underset{\underset{O}{\|}}{C}-OH \xrightarrow[\text{or } NaBH_4 (X)]{LiAlH_4} CH_3CH_2OH + H_2O$

- $CH_3-\underset{\underset{O}{\|}}{C}-Cl + H \xrightarrow[NaBH_4]{LiAlH_4} CH_3CH_2OH + HCl$

- $CH_3-\underset{\underset{O}{\|}}{C}-OR + H \xrightarrow{LiAlH_4} CH_3CH_2OH + R-OH$

esterification

- $R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R' + H \xrightarrow[NaBH_4]{LiAlH_4} RCH_2OH + R'CH_2OH$

ester

*** NOTE:**
- $NaBH_4$ do not reduce acid and its derivative namingly esters.

*** NOTE:**
- Reduction of Amide in presence of Lithium Aluminium Hydride ($LiAlH_4$) gives Alkylamine.

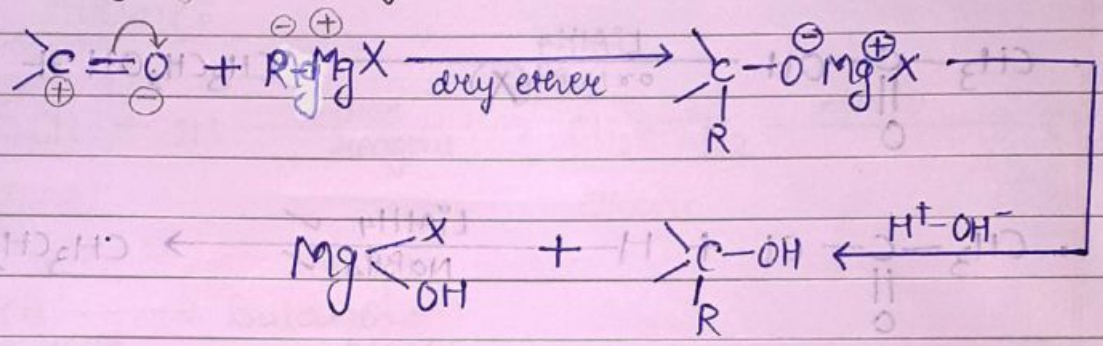
$CH_3-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow{LiAlH_4} CH_3CH_2NH_2 + H_2O.$

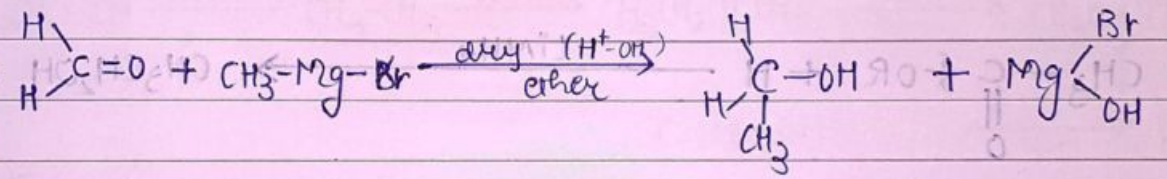
7.) From Alkyl Amine:

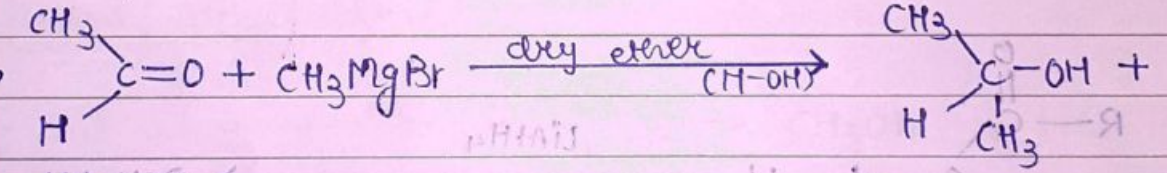
- $R-NH_2 \xrightarrow{NaNO_2 + HCl} R\{N_2\}Cl \xrightarrow{-N_2\ -Cl_2} R^{\oplus} \xrightarrow{aq\ KOH} R-OH$

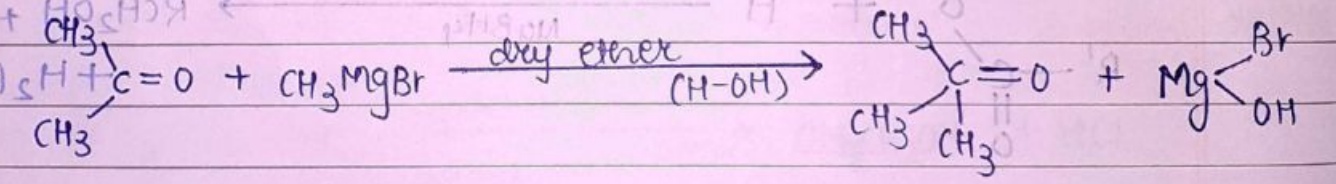
  unstable — carbocation

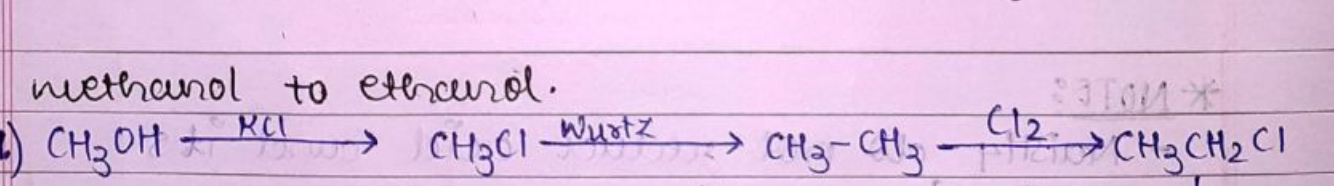
8.) From Grignard Reagent:

- 

- 

- 

- 

- 

Q:4 methanol to ethanol.

→ i) $CH_3OH \xrightarrow{HCl} CH_3Cl \xrightarrow{Wurtz} CH_3-CH_3 \xrightarrow{Cl_2} CH_3CH_2Cl \xrightarrow{KOH} CH_3CH_2OH$

ii) $CH_3OH \longrightarrow CH_3Cl \xrightarrow{KCN} CH_3CN \longrightarrow CH_3COOH \xrightarrow{LiAlH_4} C_2H_5OH$

Q:5 ethanol to methanol.

→ $CH_3CH_2OH \xrightarrow{KMnO_4} CH_3COOH \xrightarrow{Na} CH_3COONa \xrightarrow{NaOH + CaO} CH_4$ (Kolbe elec.)

$CH_4 \xrightarrow[h\nu]{Cl_2} CH_3Cl \xrightarrow{KOH} CH_3OH$

Q:6 (I) $CH_2{=}CH_2$ to P-cresol

(II) 2 Butene to ethanol.

→

*** NOTE:**

- to identify good leaving group then leaving group's conjugated acid decides it.
- leaving group's conjugated acid's strength ↑ leaving grp↑.

eg: I^- and F^- ∴ CA for $I^- = HI$ & for $F^- = HF$

best leaving ∴ $HI > HF$ ∴ $I^- > F^-$.

*** Industrial method for preparation of methanol: [WOOD SPIRIT]**

- it is obtained by destructive distillation of wood.
- after the completion of distillation we get "PYROLIGNEOUS ACID".
- composition for pyroligneous acid is:

$10\%\ CH_3COOH + 5\%\ CH_3OH + 0.5\%\ CH_3COCH_3$

acetic acid, methanol, acetone

- at very high temperature and in absence of air, distillation is carried out knowingly DESTRUCTIVE DISTILLATION.

1.) **WOOD SPIRIT**

destructive distillation.

- Volatile Subs.
  - Volatile gas: $[CH_4, CO_2, CO, N_2]$
  - Volatile liquid
    - Upper layer (Pyroligneous Acid)
      - $Ca(OH)_2$
        - $(CH_3COO)_2Ca$
        - CH_3OH + Acetone
          - Fractional disti.
            - @ 56° → Acetone
            - @ 65° → Methanol.
    - Lower layer (Wood tar) (black)
      - ↳ used as oil paint
      - ↳ protect wood
- Non Volatile Subs.: [Black charcoal]

2.) **By Catalytic hydrogenation of CO:**

$$CO + 2H_2 \xrightarrow[573-673\,K]{ZnO-Cr_2O_3,\ 200-300\ atm} CH_3OH$$

*NOTE:
- methanol is a colourless liquid boiling at 337 K.
- it is highly poisonous and drinking it can cause blindness or may lead to death.
- uses: • solvents in paints • varnishes • making of formaldehyde.

* Industrial method for preparation of Ethanol:

1.) Grain Alcohol:

- it is prepared from wash (10%-15% ethanol).

Wash (10%-15% ethanol) —coffey's distillation→ Raw spirit (90% C_2H_5OH) —Fractional dist.→ (>27°C) Aldehyde; Rectified spirit [95.5% C_2H_5OH] —CaO (quicklime)→ Lime spirit [97%] —Ca/Na metal→ Absolute Alcohol [100%]

⟹ Preparation of Wash:

A.) From Cane Sugar:

Cane Sugar —crushing→ Molasses (dark brown) —Sucrase/Invertase→ Sucrose $C_{12}H_{22}O_{11}$ (disaccharide) —sucrase/invertase (yeast)→ Glucose + Fructose ($C_6H_{12}O_6$ + $C_6H_{12}O_6$)

food of yeast: Ammonium Sulphate

Fructose —zymase (from yeast)→ $C_2H_5OH + CO_2\uparrow$ (Wash 10%-15%)

B) From Starch:

Starch —diastase enzyme (from germinated Barley)→ Maltose $C_{12}H_{22}O_{11}$ (disaccharide) —Maltase→ Glucose + Glucose ($C_6H_{12}O_6$ + $C_6H_{12}O_6$) —zymase (from yeast)→ $CO_2\uparrow + C_2H_5OH$ Wash [10%-15%]

* Yeast food: Ammonium Sulphate $(NH_4)_2SO_4$