

CHAPTER :-

ALCOHOLS, PHENOLS AND ETHERS

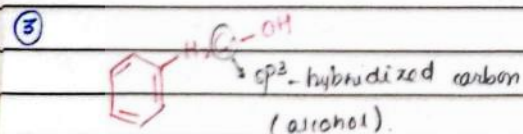
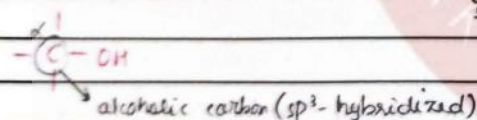
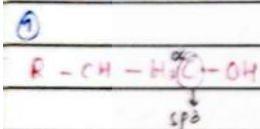
Alcohols :- hydroxy derivatives of alkanes / alkyl derivatives of H_2O .

Phenols :- hydroxy derivatives of benzene

→ Distinguishing Alcohols and Phenols:-

R-OH :-

OH is bonded to sp^3 -hybridized carbon



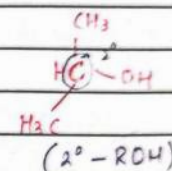
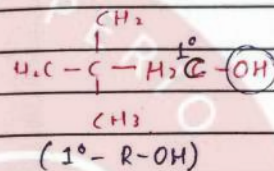
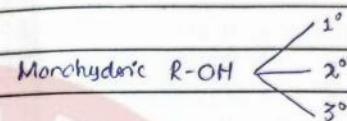
→ Ar-OH

OH bonded to sp^2 -hybridized carbon; then it is a

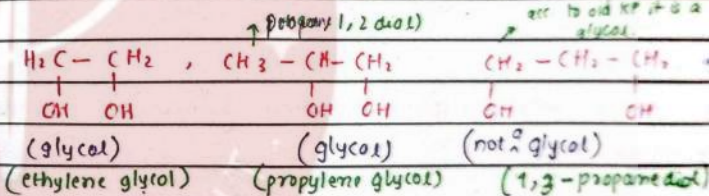
phenol. (and sp^2 -hybridized carbon is a part of benzene ring)

→ Classification of Alcohols:

1. Monohydric Alcohols :- (having one OH group)

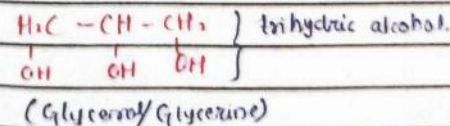


2. Dihydric Alcohols :- (having 2 -OH groups)



Glycol → a dihydric alcohol
 must have OH groups on the adjacent C-atoms.

3. Polyhydric Alcohols :- (having more than two OH groups)



→ As glucose and fructose have OH groups along

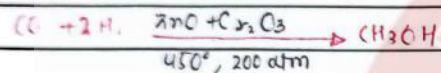
with aldehyde and ketone therefore they can also be included in alcohol family.

→ Methanol:

→ also called:

- i) CH_3OH ii) methyl alcohol iii) carbinol
- iv) wood spirit.

→ can be prepared by;



→ Ethanol

→ also called;

- i) $\text{C}_2\text{H}_5\text{OH}$ ii) ethyl alcohol iii) spirit of wine
- iv) grain alcohol.

→ most commonly occurring alcohol.

→ Before WW-II, 75% of ethanol was prepared by fermentation but now less than 10% is prepared by this method.

Fermentation:

- i) a biochemical process
- ii) occurs in the presence of enzymes
- iii) enzymes :- secreted by yeast. (no yeast, no enzyme,

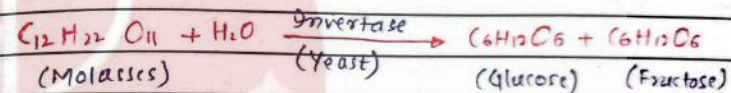
In yeast
↳ can secrete 33 imp enzymes.

- iv) Anaerobic process
- v) exothermic process.

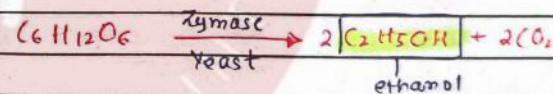
Necessary Conditions:- (for fermentation)

- i) Proper aeration (if O_2 level inc, aerobic respiration occurs)
- ii) dilution of solution (enzymes become inactive in the concentrated soln)
- iii) Optimum temperature ($25^\circ\text{C} - 35^\circ\text{C}$)
- iv) absence of any preservative [preservatives kill micro-organisms (yeast)]

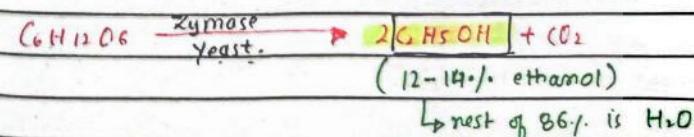
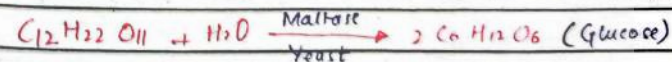
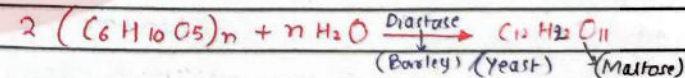
From Molasses;



FG isomers of each other

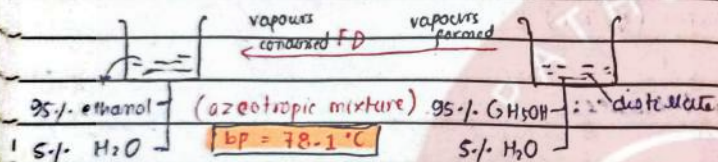
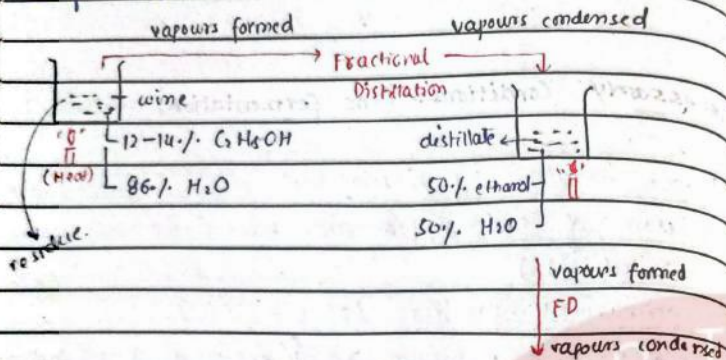


From Starch (Potato, Barley and Maize) → main sources.

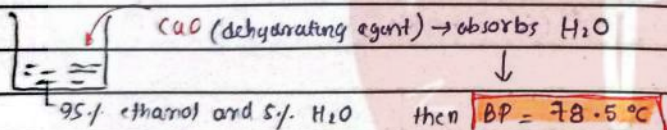


Checked By: _____

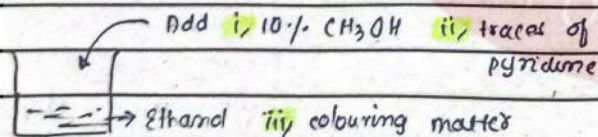
Rectified Spirit:



if the conc. of the components remain the same, they can't be separated by fractional distillation.



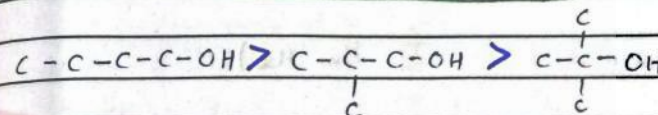
Methylated Spirit:- (Denatured Spirit)



this whole mixture is called "methylated spirit."

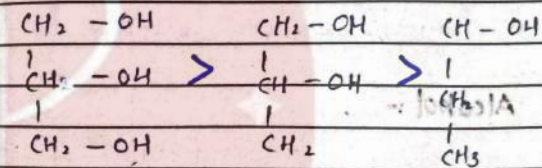
Boiling Point of Alcohols:

BP $\propto$ molecular mass $\propto$ No. of R groups



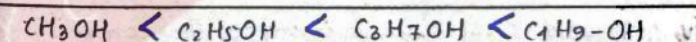
more R groups, least surface area, least IMF and hence least boiling point.

BP $\propto$ No. of Hydrogen bonds (No. of OH groups)



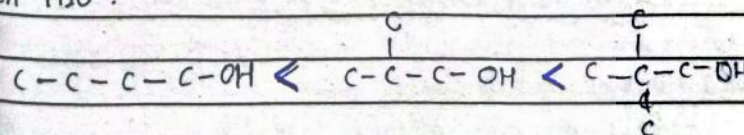
more OH groups so more H-bonds.

BP $\propto$ molecular mass



Solubility:-

In H₂O:



Checked By: _____

M T W T F S

DATE: 7/130

$C-C-C-C-OH$ (greater non-polar surface area, greater non-polar character and least solubility in H_2O .)

Solubility $\propto$ No. of $\bar{O}H$

Solubility $\propto \frac{1}{\text{molecular mass}}$

Solubility $\propto$ No of branches

In Non-Polar Solvents:-

$1^\circ > 2^\circ > 3^\circ$ (in ether)

$\rightarrow$ (least molecular mass) $\rightarrow$ smaller non-polar chain.

Reactivity of Alcohols:-

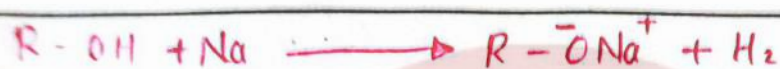
Characteristic Rxns:-

- 1) Elimination rxns (produces alkenes)
- 2) SN rxns (produces substitution products)
- 3) Electrophilic substitution rxns

① C-H bond breaking

↳ acid-base rxn (shows acidic nature)

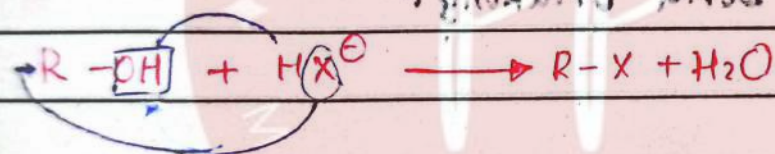
↳ electrophilic substitution rxn



② C-O bond breaking:-

↳ shows the basic nature

↳ SN rxn



③ C-H(β) and C-O breaking:

↳ β -elimination / 1,2-elimination (reactivity order $3^\circ > 2^\circ > 1^\circ$)

④ C-H(α) and O-H breaking; α -elimination

↳ oxidation rxn

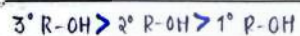
Reaction in which C-O bond breaks

Rxn in which O-H bond breaks.

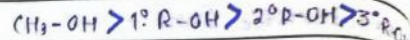
* If a nucleophile attacks on an R-OH, C-O bond breaks and a carbocation is formed.

* If an electrophile attacks, the O-H bond breaks & an alkoxide ion is formed.

Order of Reactivity:

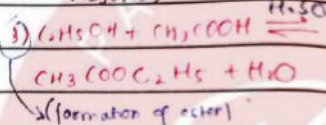
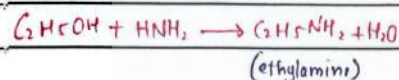
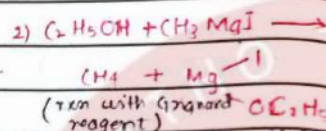
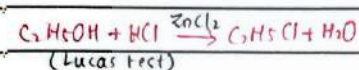
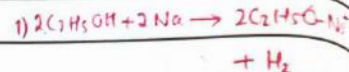
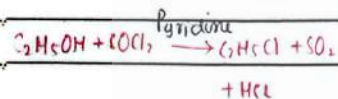


Order of Reactivity:



Rxn's:

Rxn's



Reactions of Alcohol:-

→ Due to O-H bond breaking:-

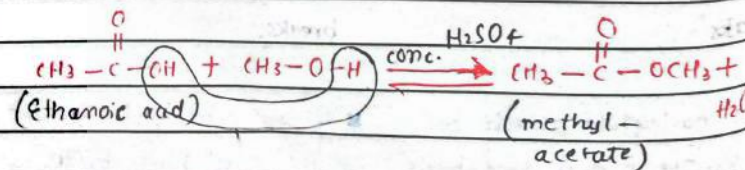
1. Esterification:

→ formation of ester

→ 'H' for H₂O formation comes from ethanol and OH from acetic acid (carboxylic acid)

→ called as Fischer Esterification

→ a type of condensation rxn.



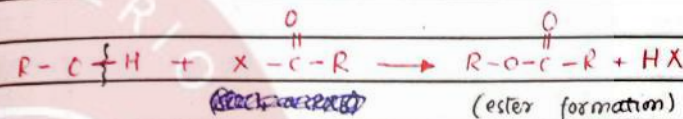
→ It is reversible and the position of equilibrium lies slightly to the product side when reactants are simple R-OH and R-COOH.

→ Order of reactivity of R-OH

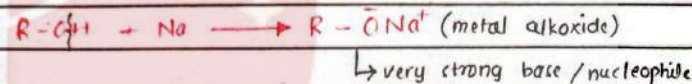
→ for steric reasons, the order of reactivity is given as:



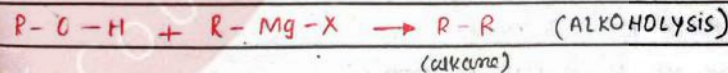
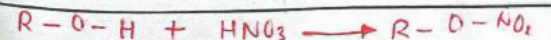
ii) Rxn with acid halide:



iii) Rxn with reactive Metal:

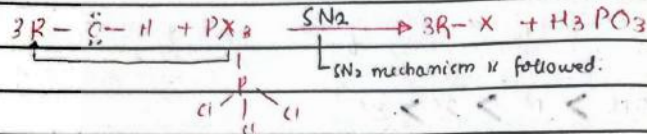


iv) Rxn with Grignard Reagent:

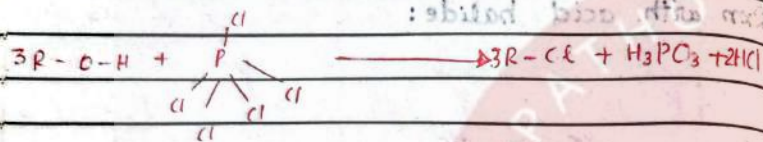
v) Rxn with H₂SO₄ / Δ:vi) Rxn with HNO₃ / Δ:

→ Rxn Due to C-O Bond Breaking:

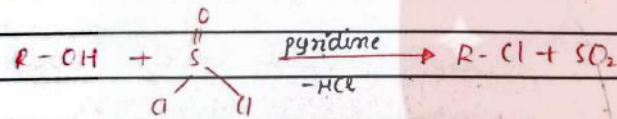
i) Rxn with PX_3 : (Phosphorus trihalides):



→ Rxn with PX_5



ii, Rxn with $SOCl_2$: : $SOCl_2$ is a better nucleophile than Cl^- .



SN₂ mechanism is followed.

In these first 3 rxns,

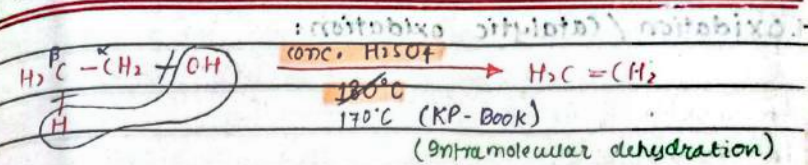
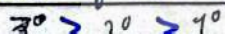
R-OH act as initial nucleophile

X^- is the main nucleophile.

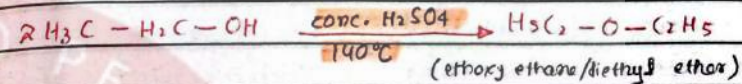
iii, condensation rxn / acid-catalyzed dehydration rxn:

→ Intermolecular dehydration

→ Order of rate of dehydration of R-OH

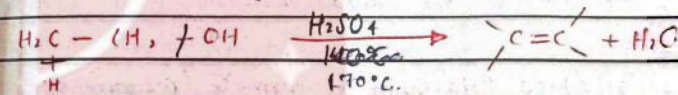


→ elimination rxn
→ acid-catalyzed dehydration.
→ unimolecular dehydration
→ breaking of C-O and C-H bond



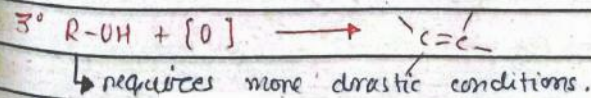
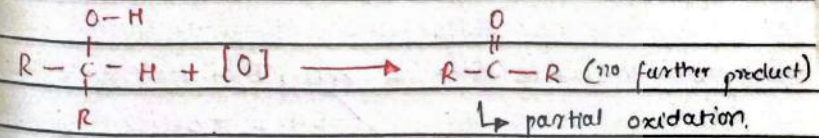
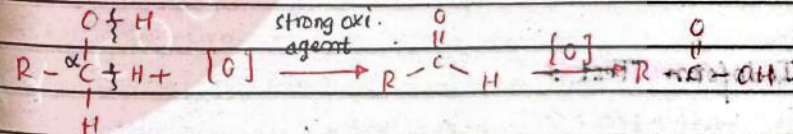
→ condensation rxn
→ inter-molecular dehydration (b/w two molecules)

(c) C-O and C-H bond breaking: (β-1,2-elimination rxn)



→ Intramolecular dehydration (within the molecule)

(d) O-H and C-H breaking (of same carbon): (α-hydrogen) (oxidation rxn)



1. Oxidation

- ↳ addition of O_2
- ↳ removal of H_2
- ↳ loss of e^-

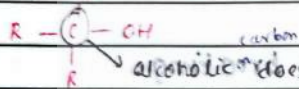
alcohol $\xrightarrow{[O]}$ carbonyl compounds $\xrightarrow{[O]}$ $COOH$

1° alcohol $\longrightarrow$ aldehyde

2° alcohol $\longrightarrow$ ketones

3° alcohol $\longrightarrow$ resistant to $[O]$.

↓ R $\longrightarrow$ undergo elimination and forms alkenes



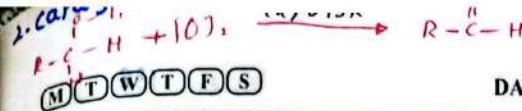
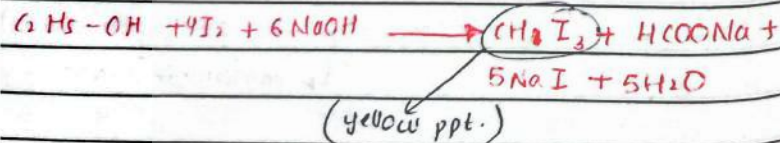
alcoholic $\longrightarrow$ does not have α (hydrogen) $\longrightarrow$

$\longrightarrow$ no α -H, no oxidation.

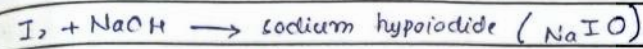
Reagent :- acidified Potassium dichromate / permanganate
 $K_2Cr_2O_7 / H_2SO_4$ $KMnO_4$.

(moder error for) given bond H- $\rightarrow$ bond O- $\rightarrow$
 Book Pg (KP) 206 + 207.

Iodoform Test :-



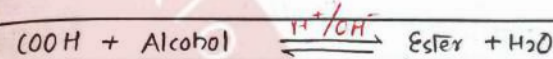
Alcohols having only one (necessary min. 1) methyl group at α -carbon will show +ve iodoform test.



$NaIO \longrightarrow$ strong oxidizing agent

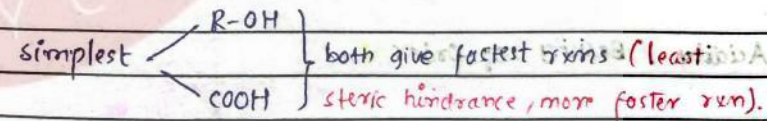
↳ carries out the oxidation of $R-OH$ and forms acetaldehyde which converts back to CH_3I (yellow ppt).

ESTERIFICATION :-

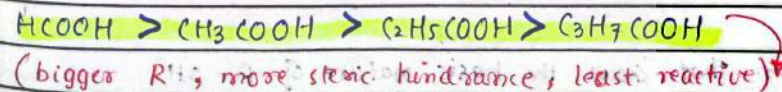


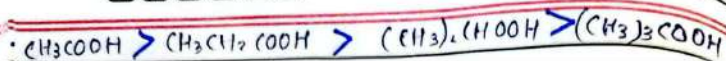
- 1° OH bond breaking of $R-OH$
- then C-O bond breaking of $COOH$.
- $R-OH$ acts as a nucleophile.
- catalysed by acid/base.
- rxn proceeds towards completion in basic media.
- exist in equilibrium in acidic media.
- in aqueous form; very slow or almost no rxn.

$\rightarrow$ Reactivity Order :-

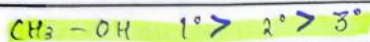
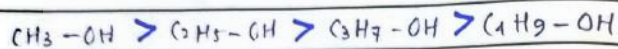


$\rightarrow$ For same $R-OH$ and different acids;

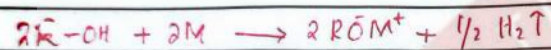




→ For same RCOOH and diff. R-OH :



→ Acidity / Basicity of Alcohol:

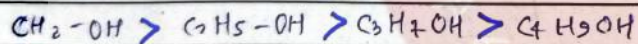


Order of Reactivity of Alcohols with Reactive Metal (Cu, Zn, Na, Ca, Mg etc).



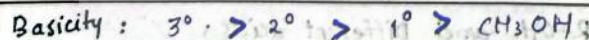
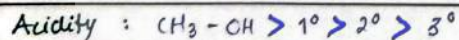
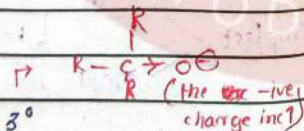
↓
strongest acid
weakest base

weakest and
strongest base (more $\bar{e}$
donating effect)

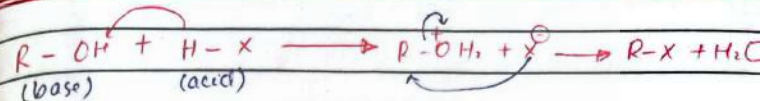


↳ smallest R (least e-donating effect)

Acidity / Basicity of Oxide



Rxn that shows the basic nature of R-OH
(C-O bond breaking) (Lucas test) :-



Acidity $\propto$ e^- -withdrawing group

Acidity $\propto$ 1

e-donating groups (OH , R , NH_2)

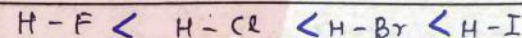
Basicity $\propto$ $\bar{e}$ -donating groups

Basicity $\propto 1$

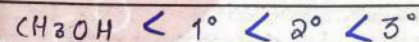
$\bar{e}$ -withdrawing groups (CN, NO, ...)

General Order of reactivity of alcohol:-

⑦ same alcohol diff. HX;

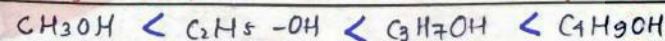


② same HX diff. Alcohol:



(strongest acid)

(strongest base)



Lucas Test :-

→ used to different alcohols.

→ Lucas Reagent :- Anhydrous $\text{ZnCl}_2 + \text{HCl}$.

MTWTFSS

DATE: 17/10

1. $\text{HI}, \text{HBr} \rightarrow$ give fast rxn
 $\rightarrow$ no need of catalyst.

$\text{HF}, \text{HCl} \rightarrow$ slow rxn
 $\rightarrow$ need a catalyst

$1^\circ \text{R-OH} + \text{LR} \rightarrow$ very slow (no rxn at RTP)
 (weakest base)

$2^\circ \text{R-OH} + \text{LR} \rightarrow$ intermediate speed
 (5 to 10 mins)

Result:- i, oily layer formation

ii, formation of cloudy appearance

alkyl halide: turbid appearance

$3^\circ \text{R-OH} + \text{LR} \rightarrow$ Fastest rxn (immediately)

Results:- i, oily appearance

ii, cloudy appearance

iii, turbidity.

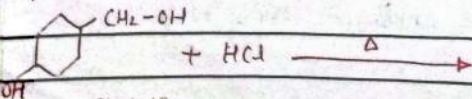
MIC: An unknown alcohol is treated with Lucas

Reagent. WOF give faster rxn and by what mechanism.

(A) $3^\circ (\text{SN}_1)$ (B) $1^\circ (\text{SN}_1)$ (C) $2^\circ (\text{SN}_1)$

(D) $3^\circ (\text{SN}_2)$

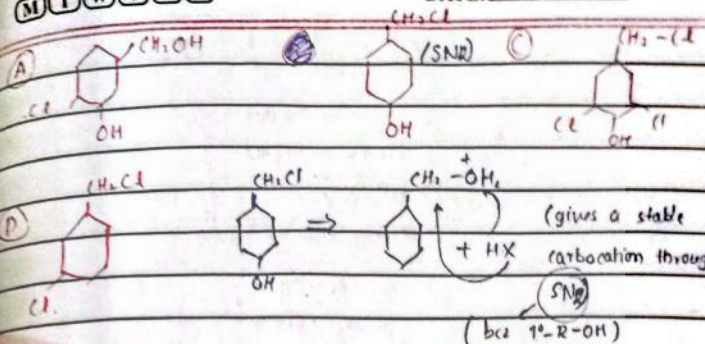
MIC: WOF is the main product of



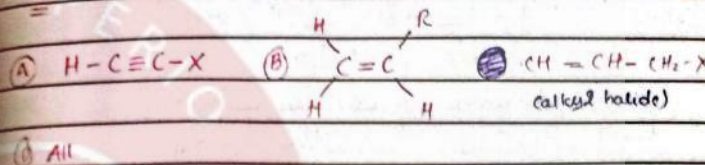
Checked By: _____

MTWTFSS

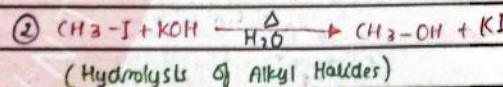
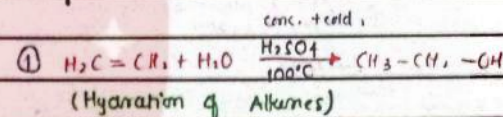
DATE: 18/10



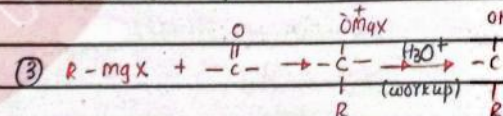
MIC: WOF give SN rxn more easily?



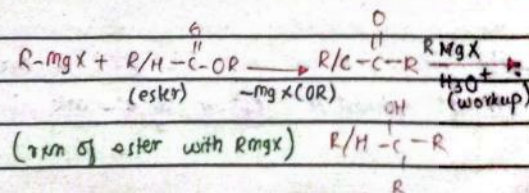
Preparation of Alcohols:



Alcohol

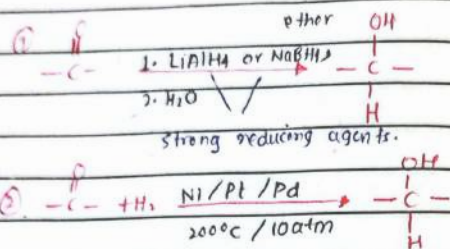


formaldehyde $\rightarrow 1^\circ \text{R-OH}$ and ketone $\rightarrow 3^\circ$
 other aldehydes $\rightarrow 2^\circ \text{R-OH}$ (Rxn of R-MgX with carbonyl compounds)



Checked By: _____

formate ester $\rightarrow$ 2° and higher esters $\rightarrow$ 3°



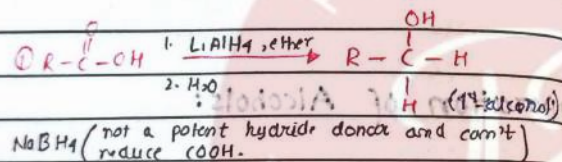
formaldehyde $\rightarrow$ CH₃-alcohol

Alcohols

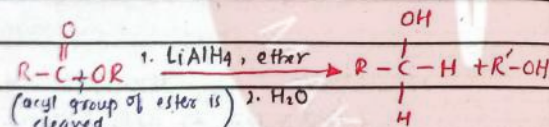
higher aldehydes $\rightarrow$ 1° alcohol

ketones $\rightarrow$ 2° alcohol.

(Reduction of carbonyl compounds)



(Reduction of COOH).



(Reduction of Esters)

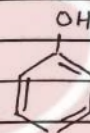
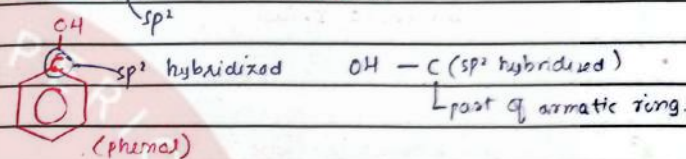
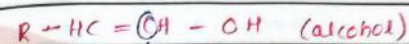
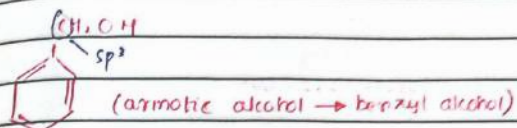
PHENOLS :-

$\rightarrow$ hydroxy derivatives of benzene

$\rightarrow$ the compound in which OH group is directly attached to sp²-hybridized carbon of aromatic ring.

Due to H-bonding of comparable molecular mass. Above 65°C both phenol and H₂O are miscible in all proportions.

$\rightarrow$ OH can be attached to an sp²-hybridized carbon but still can't be phenol if that 'C' is not a part of aromatic.



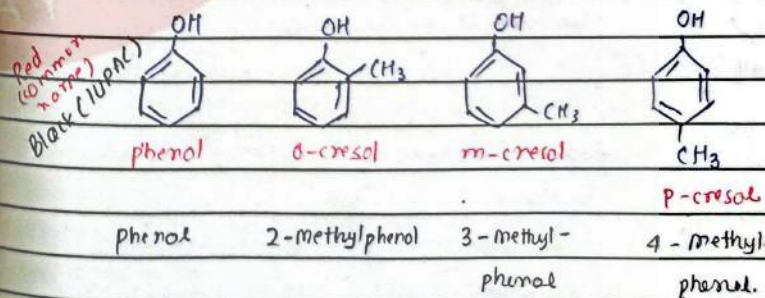
2) Carbolic acid :- (the liquid phenol containing 5% of H₂O is known as carbolic acid)

3) phenol :- (old name of benzene) used as disinfectant & germicide.

4) a compound as well as a class of OC.

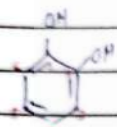
Classification of Alcohols & Phenols

1. Monohydric Alcohols :-



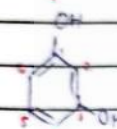
2. Dihydric Alcohols Phenols

Phenol	IUPAC NAME	COMMON NAME
--------	------------	-------------



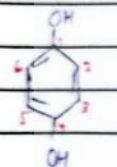
1,2-dihydroxybenzene
(benzene-1,2-diol)

catechol



1,3-dihydroxybenzene
(benzene-1,3-diol)

Resorcinol

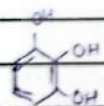


1,4-dihydroxybenzene
(benzene-1,4-diol)

Quinol
(Hydroquinone)

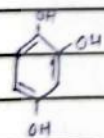
3. Trihydric Phenols

Phenol	IUPAC NAME	COMMON NAME
--------	------------	-------------



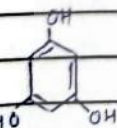
1,2,3-trihydroxybenzene

Pyrogallol



1,2,4-trihydroxybenzene

Hydroxyquinol



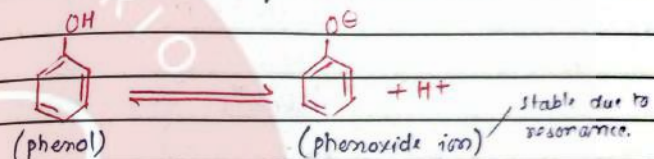
1,3,5-trihydroxybenzene

Phloroglucinol

Physical Properties:-

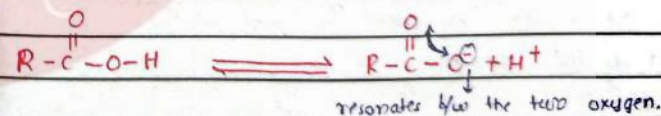
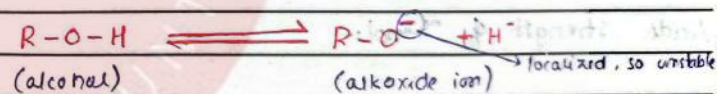
- 1) colourless liq / low MP solid at RTP.
- 2) characteristic phenolic odour.
- 3) MP = 41°C and BP = 182°C.
- 4) Sparingly soluble in H₂O at RTP i.e 25°C and completely soluble in H₂O at 68.5°C (forms pink soln).
- 5) poisonous and used as disinfectant in hospitals & washrooms.

Acidic Nature of Phenol:-



Carboxylic Acids > Phenol > Water > Alcohols

K _a	1.75 × 10 ⁻⁵	1.3 × 10 ⁻¹⁰	1.8 × 10 ⁻¹⁶	10 ^{-16 to -18}
pK _a	(5)	(10)	(16)	(16-18)



carboxylate ion > phenoxide ion > alkoxide ion

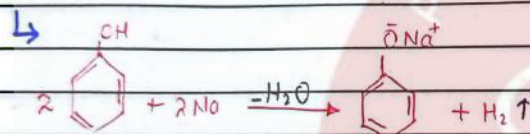
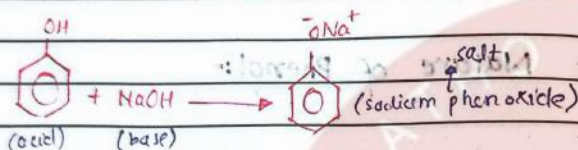
↓
more stable so its chances of formation inc↑ which in turn inc↑ H⁺ formation and hence acidity inc↑.

K_a or acidic strength

K_a or $\frac{1}{pK_a}$

PHENOLS:-

↳ dissolves in alkalis



rxn with base $\rightarrow$ forms salt
rxn with metal $\rightarrow$ forms H_2 gas is released } shows the acidic nature.

Acidic Strength of Phenol:-

- no effect on litmus paper
- doesn't evolve O_2 from O_2^{2-} and HCO_3^-
- pH of its soln is 5 or 6.

Effect of Substituents On the Acidity of Phenols:

$\bar{e}$ -withdrawing groups: $(-\text{X}, \text{NO}_2, -\text{SO}_3\text{H}, -\text{CN} \text{ etc})$

i) tends to disperse -ive charge on phenoxide ion.

- stabilize the phenoxide ion.
- increases the acidity. eg nitrophenol is more acidic than phenol.

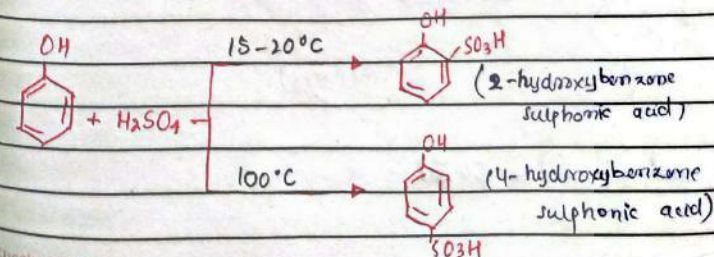
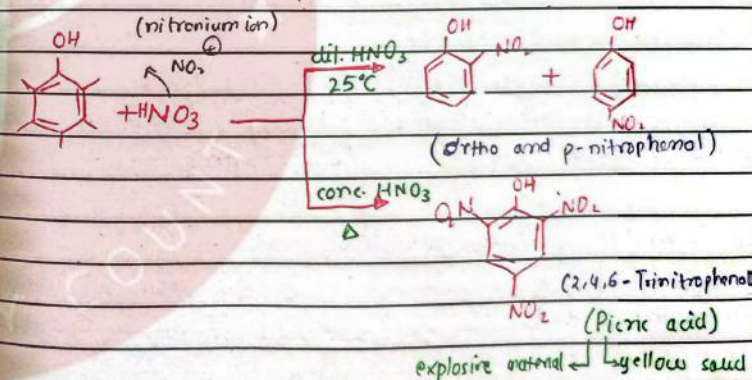
$\bar{e}$ -donating groups $(-\text{NH}_2, -\text{OR}, -\text{R} \text{ etc})$

- tends to intensify the -ive charge on phenoxide ion.
- destabilize the phenoxide ion.
- decr the acidity. e.g methyl phenol is less acidic than phenol

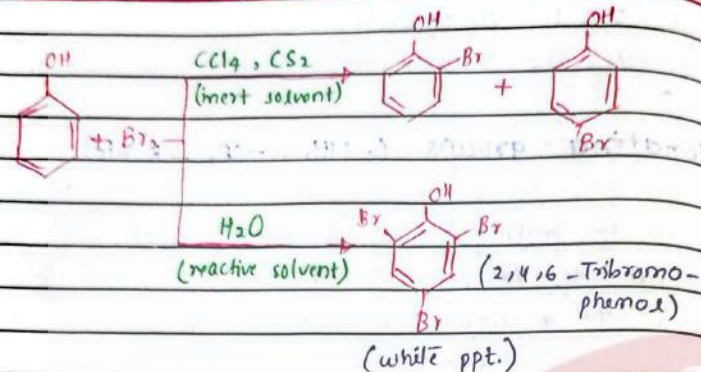
Para substituted phenol is more acidic than ortho phenol. (bcz of the intramolecular H-bonding)

Reactions of Phenol:-

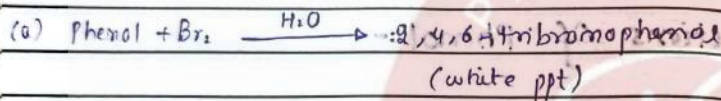
ES Rxns (in which the benzene ring is involved).



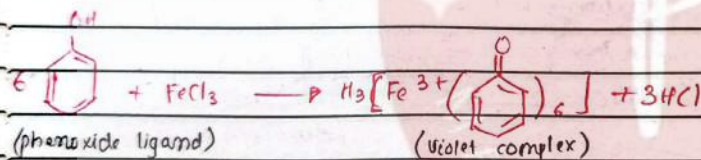
Checked By



Identification of Phenol:-

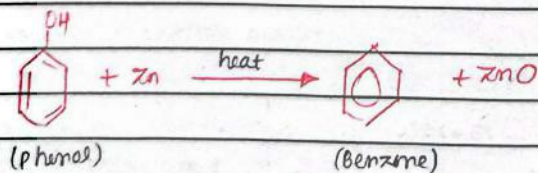


(b) Rm with FeCl₃

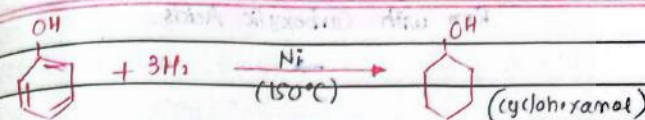


(c) Reduction of Phenol

(i) with Zn dust.



(ii) with H₂ (Ni, 150°C)



Differentiating Alcohols And Phenols:

Alcohols

Phenols

→ Hydroxy derivative of alkanes

→ Hydroxy derivatives of benzene

→ Lower alcohols are generally colourless liquids.

→ Colourless crystalline deliquescent solids

→ Less acidic (pKa = 16-20)

→ More acidic (pKa = 10)

→ Characteristic sweet smell.

→ Characteristic phenolic smell.

Br₂ - Water Test

→ No rxn with Br₂-H₂O.

→ Give white ppt. with Br₂-water.

Rxn with NaOH

→ No rxn with NaOH. (but it's a weak acid)

→ React with NaOH to form salt.

Solubility in H₂O

→ Readily soluble in H₂O

→ Sparingly soluble in H₂O at R.T.

Rxn with FeCl₃

→ No rxn.

→ Give purple ppt.

Rxn with Carboxylic Acids

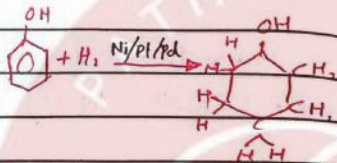
- gives esters with facility
smell. → can't react bcz both are acids.

Rxn with HX

- Lucas test → can't react

Metal Catalytic Reduction

- can't undergo catalytic reduction bcz they are already in reduced state. → forms cyclohexanol. can undergo catalytic hydrogenation.

Diazonium Salt

→ no rxn

gives
→ dyes

Rxn with a Reactive Metal

(Na, K, Mg etc.)

→ can react.

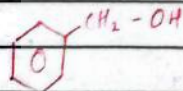
→ can react

alcohols

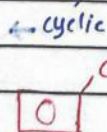
Aromatic

Aliphatic

(R-OH)



→ OH not directly attached to aromatic ring.



cyclic

non-cyclic

C-C-C-OH

(alcohol)

ETHERS

- derivatives of H₂O (diethyl) / alkory derivatives of alkanes
→ Lewis base

→ Reactivity :-

Very unstable towards -i, Disule and

ii, very strong conjugate base

iii, strong reducing agent

iv, strong oxidizing agent

Only reactive towards:

hot and conc. strong acids

oxonium ions.

Preparation:

Intermolecular dehydration of alcohols (H₂SO₄ / 140°C)

Williamson Synthesis.

