Date: 23-09-2024

Alcohols

→ When 1-H atom of alkane is replaced by OH^-, compound formed is called Alcohols or alkanols.

General formula

→ $C_nH_{2n+1}OH$

IUPAC naming

$CH_4 \longrightarrow CH_3OH$

Methyl alcohol (common name).

Methanol (IUPAC)

CH_3-CH_2-OH

ethyl alcohol (common name)

ethanol (IUPAC)

$CH_3-CH_2-CH_2-CH_2-OH$

Butyl alcohol (common name)

butanol (IUPAC)

Classification

1) Monohydric Alcohol
2) Polyhydric Alcohol

Monohydric

Alcohol containing 1 OH grp.

Date:

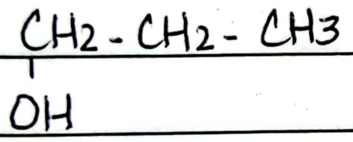
Types

- Primary alcohol
- Secondary alcohol
- Tertiary alcohol.

→ Primary alcohol

When OH is bonded with 1° carbon.

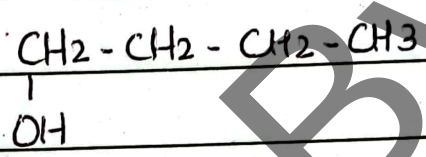
examples :



$CH_2-CH_2-CH_3$ with OH on the first carbon

Pri-propyl alcohol (C.N)

1°- propanol (IUPAC)



; $CH_2-CH_2-CH_2-CH_3$ with OH on the first carbon

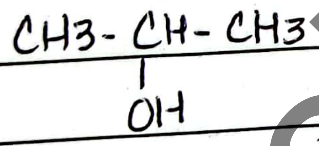
Pri- butyl alcohol (C.N)

1- Butanol (IUPAC)

→ Secondary alcohol

When OH is bonded with 2° carbon.

examples :



$CH_3-CH-CH_3$ with OH on the middle carbon

Sec-propyl alcohol (C.N)

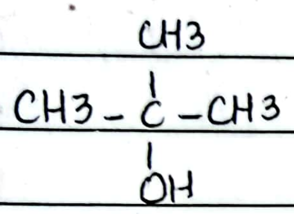
iso propyl alcohol (C.N)

2-propanol (IUPAC)

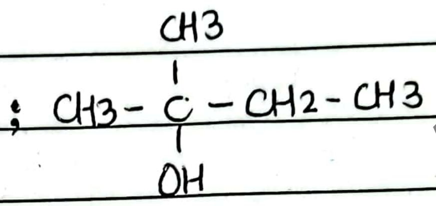
3- tertiary alcohol

When OH is bonded with 3° carbon.

example:



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



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

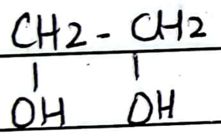
ter-butyl alcohol } (C.N)
neo-butyl alcohol } (C.N)
2-Methyl-2-propanol (IUPAC)

ter-pentyl alcohol (C.N)
2-Methyl-2-butanol (IUPAC)

→ Polyhydric alcohol

alcohol containing more than 1 OH group.

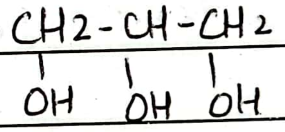
examples:



$\underset{OH}{CH_2}-\underset{OH}{CH_2}$

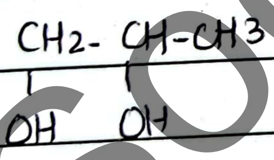
(dihydric alcohol)

- ethylene glycol (C.N)
- 1,2-ethanediol (IUPAC)



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

Glycerine / Glycerol (C.N)
1,2,3-Propanetriol (IUPAC)

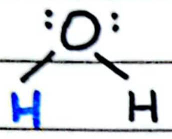


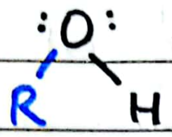
$\underset{OH}{CH_2}-\underset{OH}{CH}-CH_3$

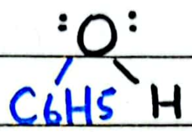
Propylene glycol (C.N)
1,2-Propanediol (IUPAC).

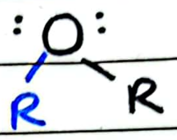
Date: 25-09-24

general comparsion


water


alcohol


phenol


ether

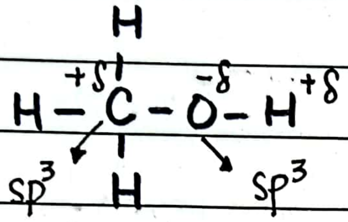
- In Alcohols, H-atom of water is replaced by alkyl group.
- In phenol, H-atom of water is replaced by phenyl group.
- In ether, 2 H-atoms of water is replaced by alkyl group.

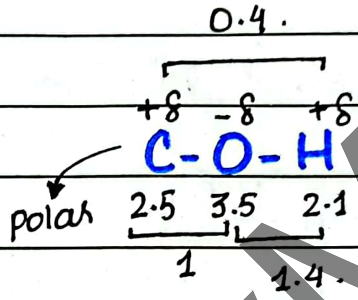
Physical Properties

- Lower alcohols (C_1-C_4) are colorless, liquids having sweet & burning taste.
- They have high melting and boiling point due to H-bonding as compared to alkanes.
- They are soluble in water due to H-bonding but lower alcohols are more soluble than higher alcohols.

Lower alcohol H-bonding > higher alcohol weak H-bonding.

Structure





- -- C-O bond, sp^3 hybridized.
- -- C-O & O-H bond polar.

acidity

- Alcohols are slightly acidic due to more electronegativity of Oxygen.

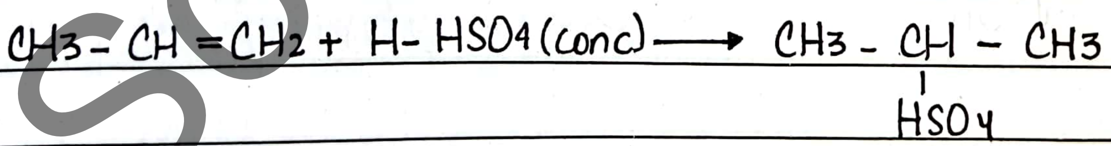
example:

$R\text{-}OH + Na \longrightarrow \overset{\text{alkoxide.}}{RO\text{-}Na} + \frac{1}{2}H_2$

$H\text{-}OH + Na \longrightarrow NaOH + \frac{1}{2}H_2.$

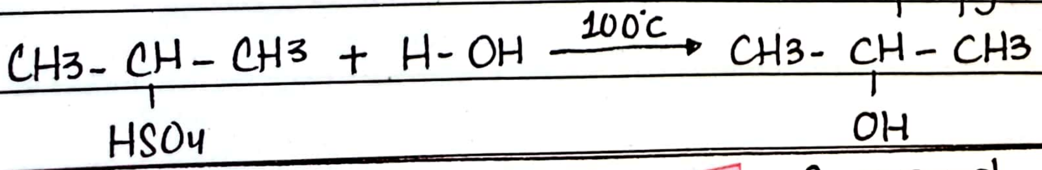
Preparation

1- hydration of alkene



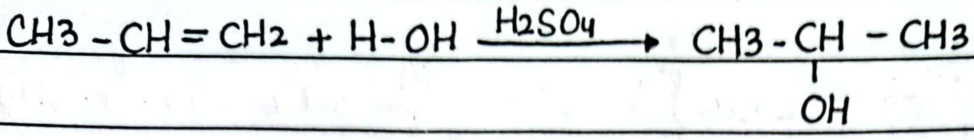
$CH_3\text{-}CH{=}CH_2 + H\text{-}HSO_4\,(conc) \longrightarrow CH_3\text{-}\underset{HSO_4}{\underset{|}{CH}}\text{-}CH_3$

sec-propyl-H-sulphate.



$CH_3\text{-}\underset{HSO_4}{\underset{|}{CH}}\text{-}CH_3 + H\text{-}OH \xrightarrow{100^\circ C} CH_3\text{-}\underset{OH}{\underset{|}{CH}}\text{-}CH_3$

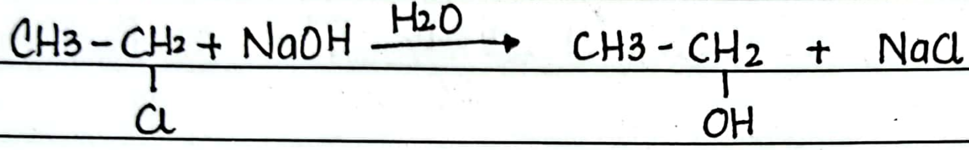
2-propanol



$$CH_3-CH=CH_2 + H-OH \xrightarrow{H_2SO_4} CH_3-\underset{\substack{|\\ OH}}{CH}-CH_3$$

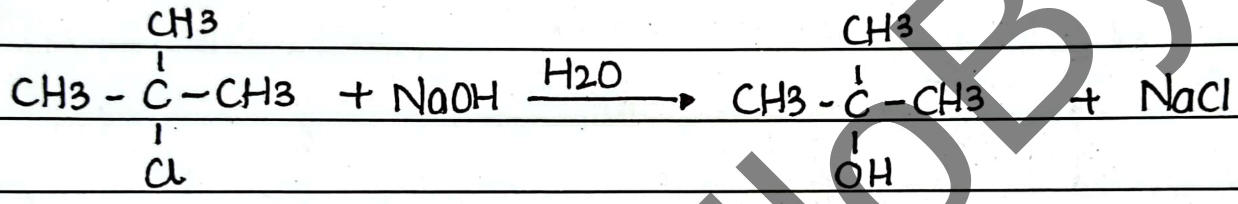
2- propanol

2- hydrolysis of alkyl halide



$$CH_3-\underset{\substack{|\\ Cl}}{CH_2} + NaOH \xrightarrow{H_2O} CH_3-\underset{\substack{|\\ OH}}{CH_2} + NaCl$$

ethanol

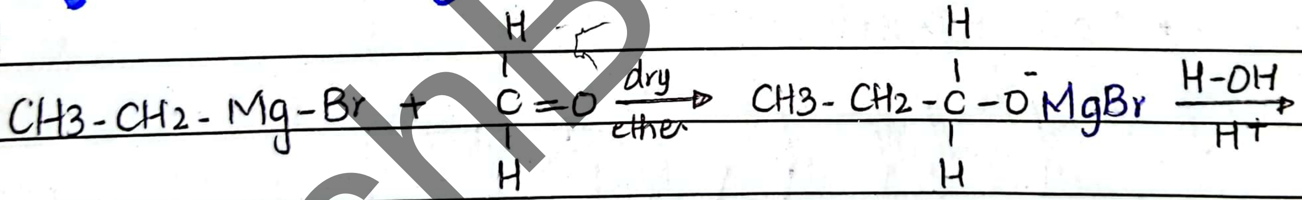


$$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ Cl}}{C}}-CH_3 + NaOH \xrightarrow{H_2O} CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ OH}}{C}}-CH_3 + NaCl$$

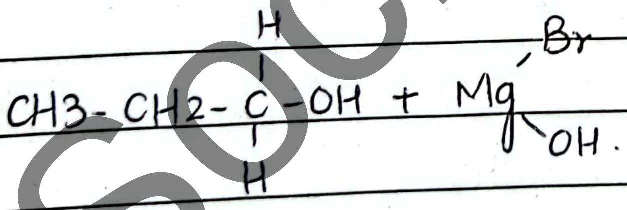
ter- butyl chloride 2-Methyl -2- propanol.

3. Grignard rxn

formaldehyde



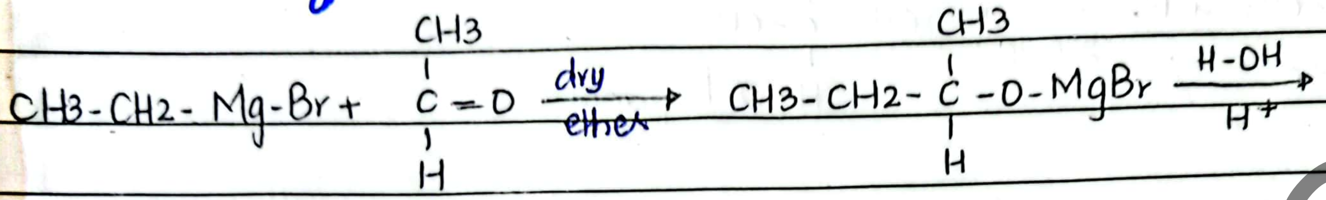
$$CH_3-CH_2-Mg-Br + \overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{C}}=O \xrightarrow[ether]{dry} CH_3-CH_2-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{C}}-O^{-}MgBr \xrightarrow[H^+]{H-OH}$$



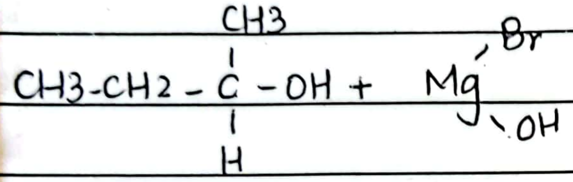
$$CH_3-CH_2-\overset{\substack{H\\ |}}{\underset{\substack{|\\ H}}{C}}-OH + Mg\genfrac{}{}{0pt}{}{Br}{OH}.$$

1- Propanol.

acetaldehyde



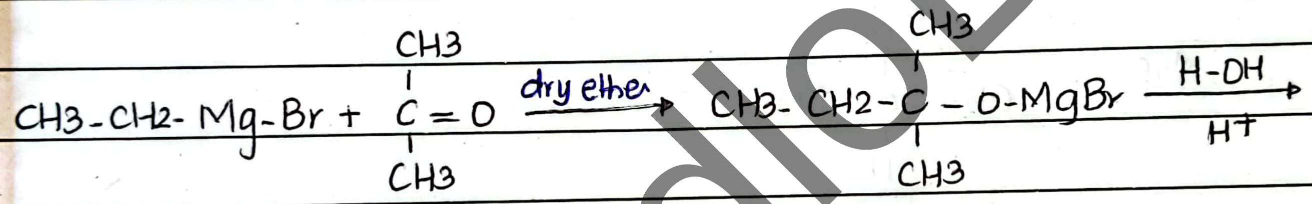
$$CH_3-CH_2-Mg-Br + \overset{CH_3}{\underset{H}{C}}=O \xrightarrow[ether]{dry} CH_3-CH_2-\overset{CH_3}{\underset{H}{C}}-O-MgBr \xrightarrow[H^+]{H-OH}$$



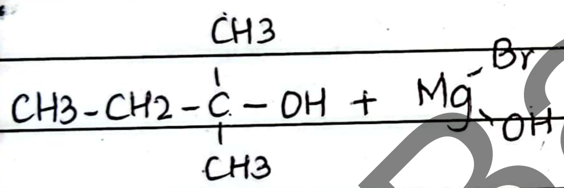
$$CH_3-CH_2-\overset{CH_3}{\underset{H}{C}}-OH + Mg\begin{smallmatrix}Br\\OH\end{smallmatrix}$$

2 - Butanol

acetone



$$CH_3-CH_2-Mg-Br + \overset{CH_3}{\underset{CH_3}{C}}=O \xrightarrow{dry\ ether} CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-O-MgBr \xrightarrow[H^+]{H-OH}$$



$$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OH + Mg\begin{smallmatrix}Br\\OH\end{smallmatrix}$$

3°_Pentanol.

4- Reduction with aldehyde and ketone

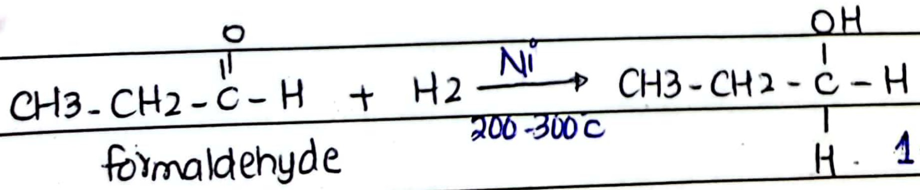
- Aldehyde is reduced to 1° Alcohol.
- Ketone is reduced to 2° Alcohol.

catalytic hydrogenation

(Ni, Pt, Pd)

Ni → 200-300°c

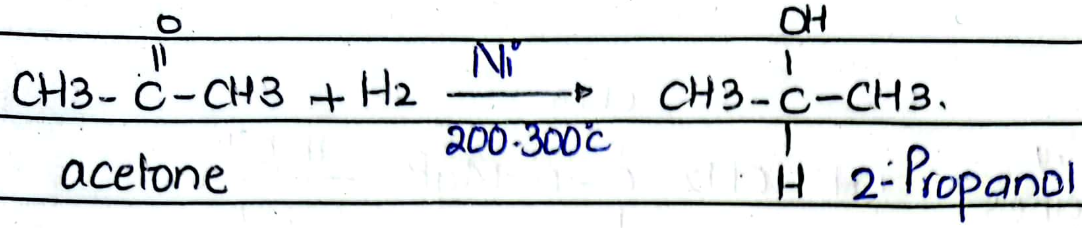
Pt, Pd → 25°C.



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + H_2 \xrightarrow[200-300^\circ c]{Ni} CH_3-CH_2-\overset{OH}{\underset{H}{C}}-H$$

formaldehyde

1-Propanol



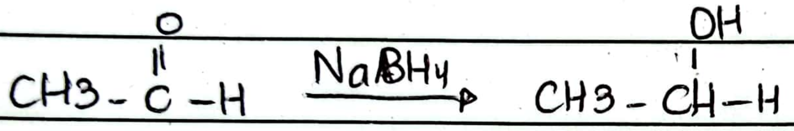
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2 \xrightarrow[200\text{-}300^\circ C]{Ni} CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3.$$

acetone

2-Propanol

reducing agent

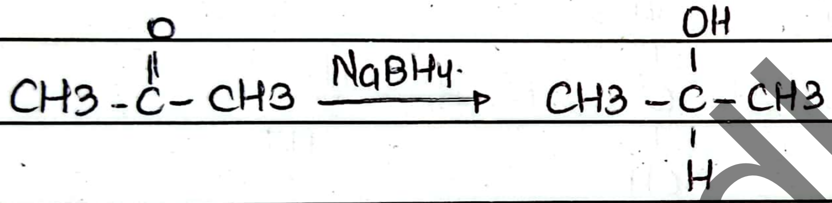
- LiAlH4
  - ↳ strong
- NaBH4
  - ↳ weak



$$CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow{NaBH_4} CH_3-\overset{\overset{OH}{|}}{CH}-H$$

acetaldehyde

1-ethanol.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaBH_4} CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

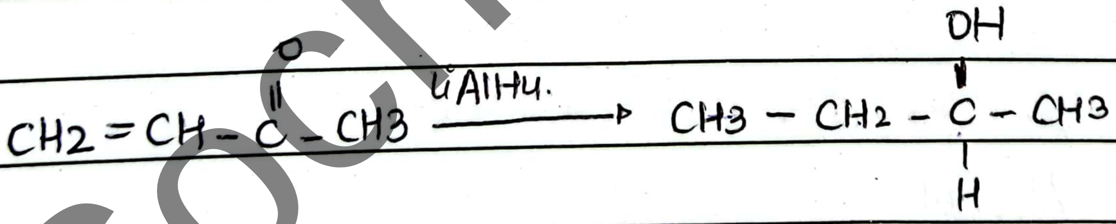
acetone

2°-Propanol.

$$CH_2=CH-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{NaBH_4} CH_2=CH-\overset{\overset{O}{\|}}{C}-CH_3$$

2- Butanone-3-ene.

2-Butanol. 3-ene.

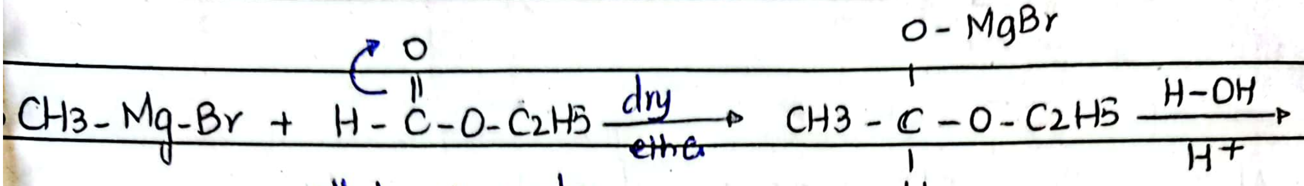


$$CH_2=CH-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{LiAlH_4} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

2-Butanone-3-ene

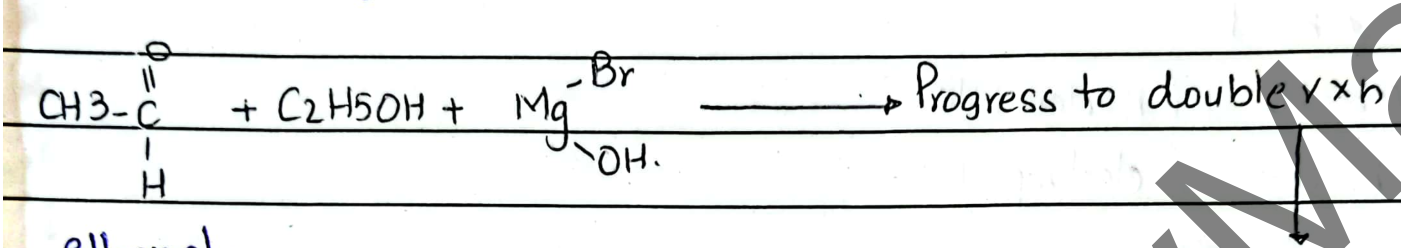
2-Butanol.

5- Ester



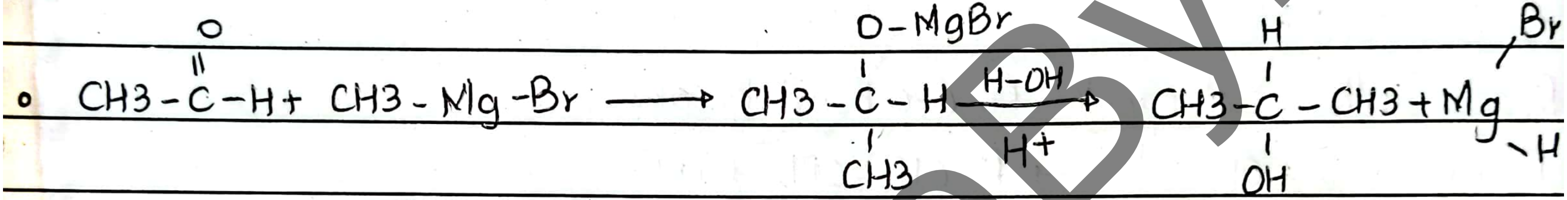
$$CH_3-Mg-Br + H-\overset{\overset{O}{\|}}{C}-O-C_2H_5 \xrightarrow[ether]{dry} CH_3-\underset{H}{\overset{O-MgBr}{C}}-O-C_2H_5 \xrightarrow[H^+]{H-OH}$$

ethylmethanoate.



$$CH_3-\underset{H}{\overset{\overset{O}{\|}}{C}} + C_2H_5OH + Mg\genfrac{}{}{0pt}{}{Br}{OH} \longrightarrow \text{Progress to double rxn}$$

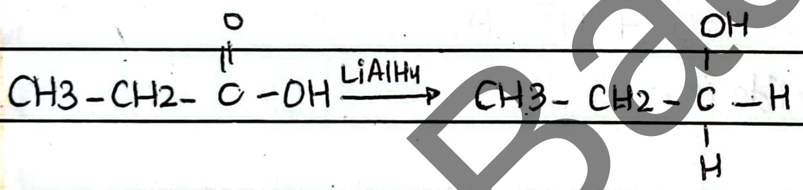
ethanal.



$$CH_3-\overset{\overset{O}{\|}}{C}-H + CH_3-Mg-Br \longrightarrow CH_3-\underset{CH_3}{\overset{O-MgBr}{C}}-H \xrightarrow[H^+]{H-OH} CH_3-\underset{OH}{\overset{H}{C}}-CH_3 + Mg\genfrac{}{}{0pt}{}{Br}{H}$$

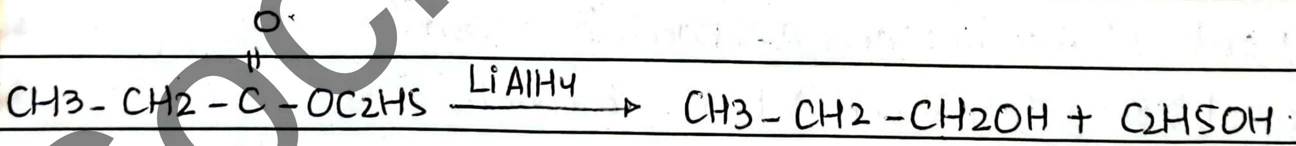
2- Propanol.

6- Reduction of COOH



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{LiAlH_4} CH_3-CH_2-\underset{H}{\overset{OH}{C}}-H$$

ethanoic acid 1-Propanol.



$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightarrow{LiAlH_4} CH_3-CH_2-CH_2OH + C_2H_5OH$$

ethylpropionate 1-propanol. ethanol

Reactivity

Reactivity of Alcohol with multiple reagents depends on 2 types of reactive bond :-

1. C-O bond (nucleophile)
2. OH bond. (electrophile).

C-O bond:

Reacts with nucleophile, so C-O bond breaks.

$$R-CH_2-CH_2-OH \xrightarrow{Nu^-} R-CH_2-CH_2^+ + OH^-$$

carbocation

O-H bond:

Reaction with electrophile so, O-H bond breaks

$$R-CH_2-CH_2O-H \xrightarrow{E^+} R-CH_2-CH_2O^- + H^+$$

alkoxide ion.

Order

"Reactivity order of Alcohol when C-O bond is broken".

Tertiary alcohol > Secondary alcohol > Primary alcohol.

Reason:

Due to stability of carbocation.

"Reactivity order of alcohol when O-H bond is broken".

CH_3-OH > Primary alcohol > Secondary OH > Tertiary alcohol.

Reason:

- less R-group leads to less stability of OH^-
- due to inductive effect of alkyl group.

"Solubility"

Lower alcohol are more Soluble than higher soluble becoz of polarity of OH decrease with increase in R-group.

MCQ

Which alcohol is more soluble Methanol

Which alcohol is good solvent Ethanol → King of Solvent

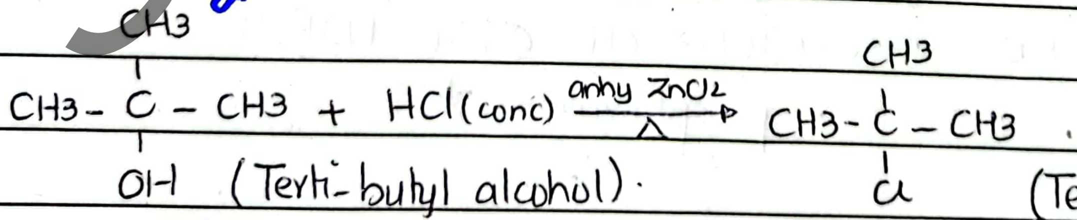
$\boxed{\text{reactivity} \propto \text{solubility.}}$

reaction when C-O bond break

1- Reaction with HX or lucas Test of identification

$$R-OH + HCl_{(conc)} \xrightarrow[\Delta]{\text{anhydrous } ZnCl_2} R-Cl + H_2O.$$

Tertiary alcohol



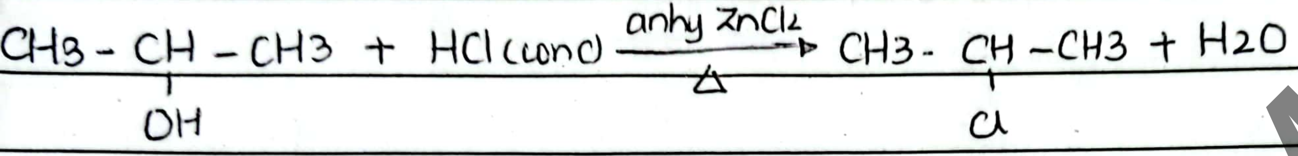
$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 + HCl(conc) \xrightarrow[\Delta]{\text{anhy } ZnCl_2} CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_3.$$

(Terti-butyl alcohol). (Ter-butyl chloride)

identification:

immediate oil layer formation.

Secondary



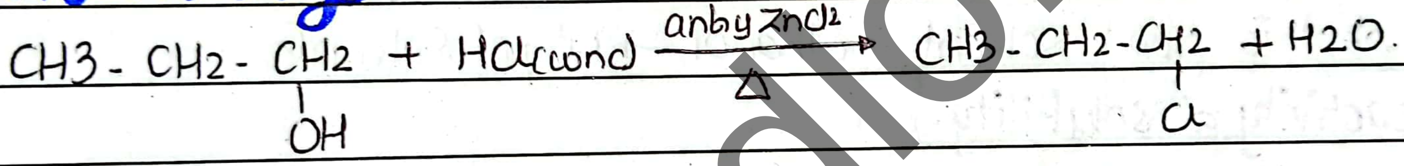
$$CH_3-\underset{OH}{CH}-CH_3 + HCl_{(cond)} \xrightarrow[\Delta]{\text{anhy } ZnCl_2} CH_3-\underset{Cl}{CH}-CH_3 + H_2O$$

Sec-propyl alcohol Sec-propyl chloride

identification:

insoluble oil layer after 5-10min.

Primary



$$CH_3-CH_2-\underset{OH}{CH_2} + HCl_{(cond)} \xrightarrow[\Delta]{\text{anby } ZnCl_2} CH_3-CH_2-\underset{Cl}{CH_2} + H_2O.$$

1-Propanol 1-chloropropane.

identification:

oil layer after heating

reaction with thionyl chloride

$CH_3-CH_2-OH + \underset{(Cl-SOCl)}{SOCl_2} \xrightarrow{\text{Pyridine}} CH_3-CH_2-Cl + SO_2 + HCl$

reaction with phosphorus halide

$3CH_3-CH_2-OH + PBr_3 \longrightarrow 3CH_3-CH_2-Br + H_3PO_3.$

phosphorus acid

$3CH_3-CH_2-OH + PI_3 \rightarrow 3CH_3-CH_2-I + H_3PO_3$.

acid catalyzed dehydration of alcohol

$CH_3-CH_2-OH \xrightarrow[180°C]{conc\ H_2SO_4} CH_2=CH_2 + H_2O$

$CH_3-CH_2-OH \xrightarrow[140°]{con\ CH_2SO_4} CH_3-CH_2-O-CH_3-CH_2$

$CH_3-CH_2-O\boxed{H + HO}-CH_2-CH_3$

reaction with ammonia

$CH_3-CH_2-OH + H-NH_2 \xrightarrow{ThO_2} CH_3-CH_2-NH_2 + H_2O$.

"Mechanism of alcohol Condensation"

Step#1 Protonation of alcohol

$CH_3-CH_2-\ddot{O}H + \underset{(H-HSO_4^-)}{H^+} \rightarrow \left[CH_3-CH_2-\underset{H}{\overset{+}{O}}-H\right]$

oxonium ion / intermediate

Step#2 attack of 2nd alcohol on carbocation

$CH_3-CH_2-\underset{H}{\overset{+}{O}}-H + CH_3-CH_2-OH \rightarrow CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 + H_2O$

Oxonium ion

Step#3 regeneration of catalyst

$CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 + H_2\ddot{O} \rightarrow CH_3-CH_2-O-CH_2-CH_3 + H_3O^+$.

$H_3O^+(H-H_2O) + HSO_4^- \rightarrow H_2SO_4 + H_2O$.

$$\overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-\overset{\delta-}{Br}+C_2\overset{\delta-}{H_5}\overset{\delta-}{OH}\xrightarrow[\Delta]{\text{dry ethe}}CH_3-CH_2-CH_3+Mg<^{Br}_{OH}$$

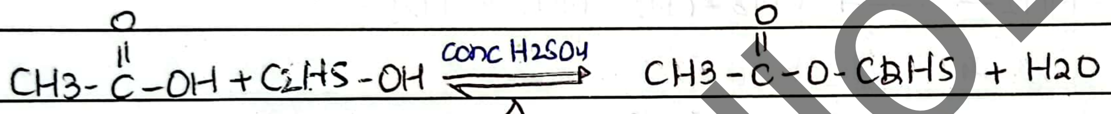
Propome.

Date:

reaction with OH breakage

reaction with COOH or Preparation of ester or identification test for COOH

When Alcohol is reacted with Carboxylic acid in presence of conc H_2SO_4 ester is formed. This Process is called Fisher esterfication.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH+C_2H_5-OH\xrightleftharpoons[\Delta]{\text{conc } H_2SO_4}CH_3-\overset{\overset{O}{\|}}{C}-O-C_2H_5+H_2O$$

methyl ethanoate }
ethyl acetate. } (Fishy smell)

williamson Synthesis

$$CH_3-CH_2-OH+Na\longrightarrow CH_3-CH_2-ONa+\tfrac{1}{2}H_2$$

Sodium ethoxide.

Grignard reagent

$$\overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-\overset{\delta-}{Br}+C_2H_5\overset{\delta-}{O}\overset{\delta+}{H}\xrightarrow[\Delta]{\text{dry ethe}}CH_4+Mg<^{Br}_{OC_2H_5}$$

methane

Page #

Teacher's Signature:

Oxidation

It can have following point:

- Addition of O
- Removal of H
- Increase in oxidation state
- loss of electrons

1- Pri-alcohol is oxidized to aldehyde which is further oxidized into carboxylic acid.

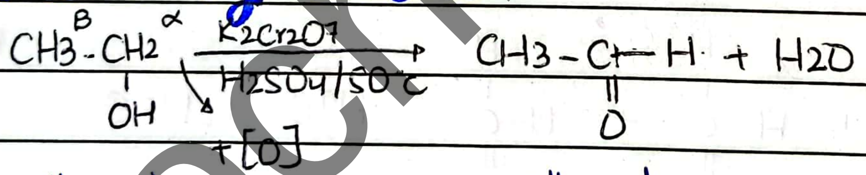
2- Sec- alcohol is oxidized to ketone which does not further oxidized becoz of no further α-H atom.

3- Ter-alcohol does not oxidize due to absence of α-H under the same condition it undergo elimination rxn.

Oxidizing agent

$K_2Cr_2O_7$ is the best oxidizing agent for alcohol.

Primary alcohol

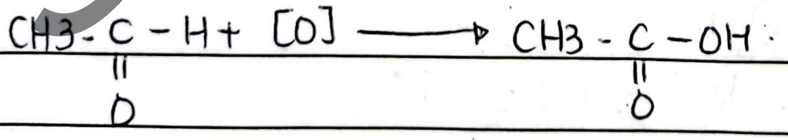


$$\overset{\beta}{CH_3}-\underset{\underset{OH}{|}}{\overset{\alpha}{CH_2}} \xrightarrow[H_2SO_4/50^\circ C]{K_2Cr_2O_7} CH_3-\underset{\underset{O}{\|}}{C}-H + H_2O$$

$+[O]$

ethanol ethanal.

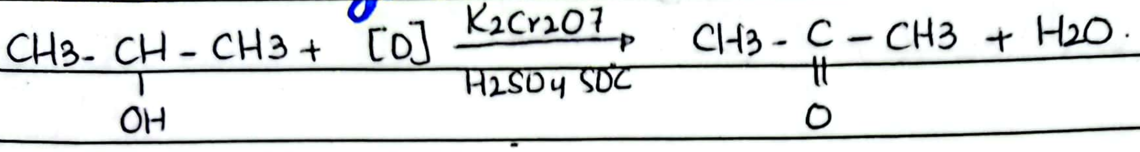
→ To stop further reaction place it in ice, if same condition continues then reaction will form COOH.



$$CH_3-\underset{\underset{O}{\|}}{C}-H + [O] \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-OH$$

ethanal ethanoic acid

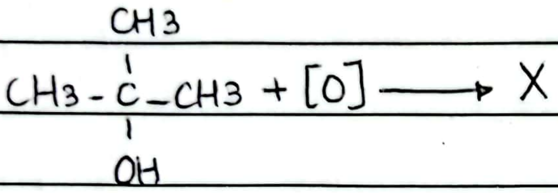
Secondary alcohol



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 + [O] \xrightarrow[H_2SO_4\ SOC]{K_2Cr_2O_7} CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + H_2O$$

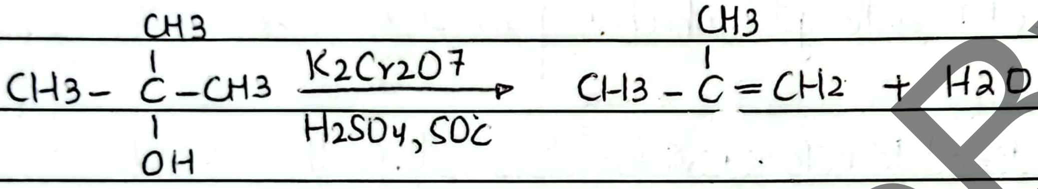
2-propanol. propanone

Tertiary alcohol



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_3 + [O] \longrightarrow X$$

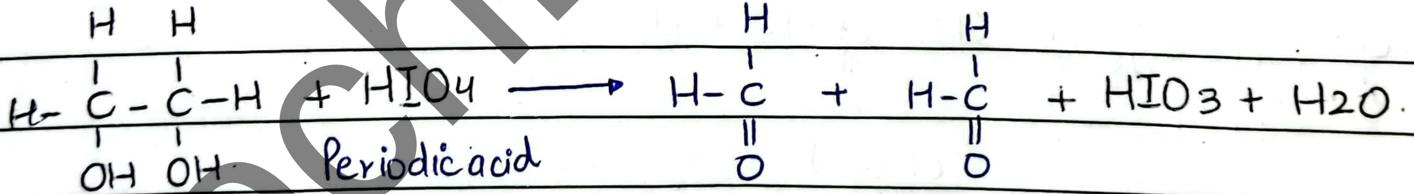
No oxidation



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-CH_3 \xrightarrow[H_2SO_4,\ SOC]{K_2Cr_2O_7} CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + H_2O$$

2-Methyl-2-Propene

oxidative cleavage of 1-2 diol



$$H-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}-H + \underset{\text{Periodic acid}}{HIO_4} \longrightarrow H-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle O}{\underset{\|}{C}}}} + H-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle O}{\underset{\|}{C}}}} + HIO_3 + H_2O$$

(glycol) Formaldehyde

- This rxn is selective for 1,2-diols
- **Confirmatory / identification test for 1,2 diol.**

Thiols → derivative

nomenclature

CH_3-OH	CH_3-SH
(Methyl alcohols)	(Methylthiolalcohol)
(Methanol)	(Methanethiol.)

Physical properties

1- weak H-bonding than alcohol.

2- Low Boiling point than alcohol

↳ because of electronegativity difference & atomic size.

Structure

R-OH	R-SH
∘ Bond length is smaller	∘ Bond length is longer
∘ O is more electronegative	∘ S is less electronegative
∘ Small size	∘ Large size
∘ more polar	∘ less polar

reactivity

Thiol are more acidic than Alcohol. becuz thiol can lose H more easily.

$Pka \propto 1/acidity$.

→ Pka of Thiol is = 10 (More acidic), (less polar)

→ Pka of alcohol is = 16-20 (less acidic), (more polar).

Oxidation

→ $R-SH \xrightarrow{oxidize} S-O$ & → $R-OH \xrightarrow{oxidize} C=O$

Date: 08-10-24.

Phenols

"Aromatic compound having one or more than one 'OH group' directly bonded with Carbon of benzene ring is called phenol."

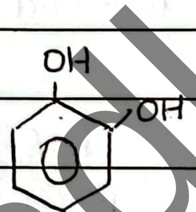
→ (Carbolic acid) is a simple example it was first obtain from coal tar by Range in 1834.

→ Phenol name is derived from old name of benzene "phene".

nomenclature

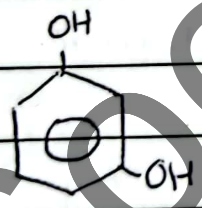
Phenol (C.N)

Carbolic acid (IUPAC)



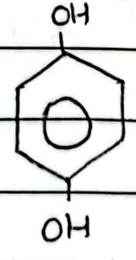
Catechol (C.N)

1,2-Dihydroxybenzene
2-Hydroxyl phenol
o- Hydroxyphenol.
(IUPAC)

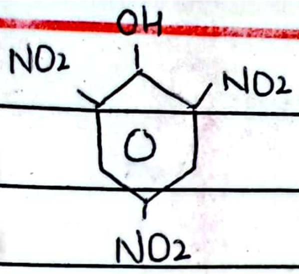


resorcinol (C.N)

1,3-Dihydroxylbenzene
3- Hydroxyphenol
m- Hydroxylphenol



Hydroquinone (C.N).
1,4- Dihydroxylbenzene (IUPAC)
4- Hydroxyl phenol, p- Hydroxylphenol



2,4,6-Trinitrophenol (IUPAC)

Picric acid (C.N).

TNP

Structure

- ★ OH is sp^2 hybridized and is bonded to sp^2 aromatic C.
- ★ The C-O & OH bond are electronegative.
- ★ The C of alcohol is sp^3 hybridized & C of benzene/phenol is sp^2.
- ★ The bond length of alcohol is larger than phenol because of conjugation & hyperconjugation.

Physical Properties

- Phenol is colorless, crystalline, poisonous solid.
- It has phenolic like smell.
- It has 41°c melting point & 182° boiling point.
- It is sparingly soluble in water forming pink solution at 25°C & completely soluble at 68.5°c
- It causes blisters on skin.
- It is used as disinfectants.
- It is deliquescent → convert into liq.

Date: 09-10-24.

acidicity of Phenol

Order:

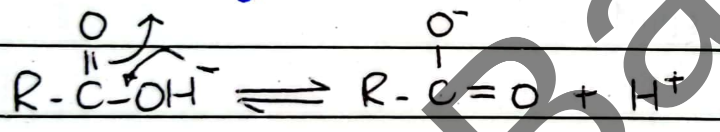
Carboxylic acid > Phenol > Alcohol.

i- $\boxed{pKa \propto \frac{1}{\text{acidic strength}}}$

- pKa of COOH = 5 (more acidic)
- pKa of C_6H_5-OH = 10 (Less acidic)
- pKa of OH = 16-20 (Least acidic)

ii- $\boxed{\text{Acidic strength} \propto \text{Stability of conjugate base}}$

Carboxylic acid

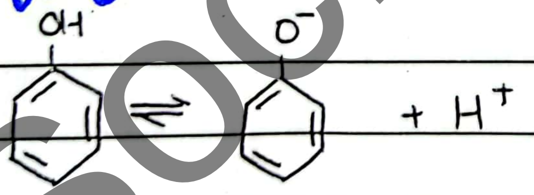


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \rightleftharpoons R-\overset{\overset{\displaystyle O^-}{|}}{C}=O + H^+$$

carboxylic acid Carboxylate ion

(–) charge is delocalized on 2 oxygen atom.

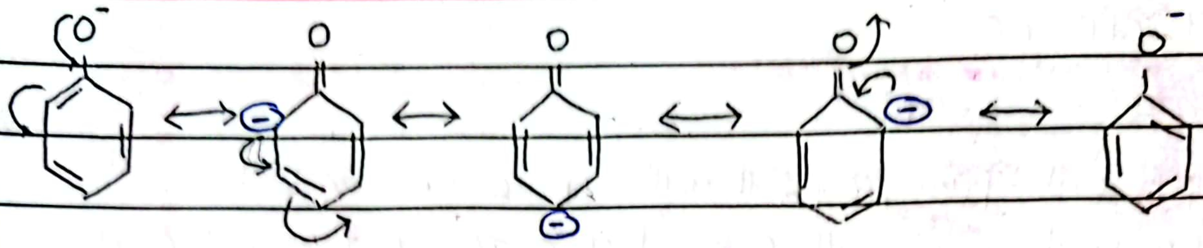
phenol



phenol phenoxide

(–) is delocalized on ortho- para position of benzene ring

Date:



alcohol

$R-OH \rightleftharpoons R-O^- + H^+$

alkoxide ion
(unstable)

Questions

i- Why COOH is more stable than phenol?

Carboxylate ion is more stable than phenoxide ion because negative charge is delocalized on 2 oxygen atom.

ii- Why phenol is more stable than alcohol?

Phenoxide ion is more stable & possess the property of delocalization, which is not present in alcohol making its ion less stable.

effect of substituent on activity of Phenol

meta-directing group

The meta-directing groups are **electron with-drawing group**. These catches or withdraws electron from benzene ring making the overall bond of C weaker, same in case of C-H bond. The withdrawing effect causes the H to be easily losen making it more acidic. Stabilizes conjugate base.

Page #

Teacher's Signature:

$COOH$, SO_3H, CHO, CO.

ortho - para group

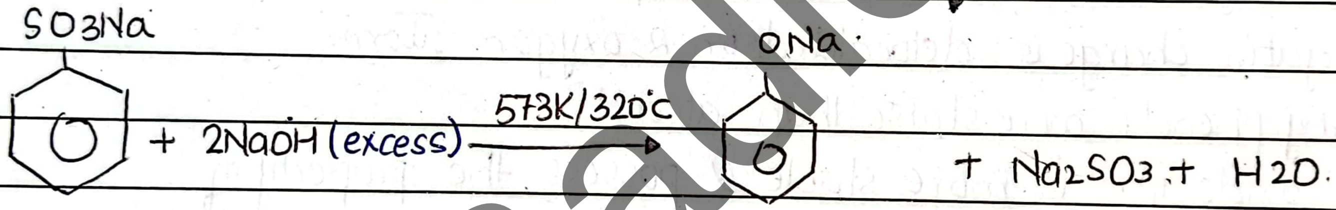
If the group is orth - para group, it will donate electron to the benzene ring making overall C bond stronger, in terms of C-H so it will definently not going to lose H easily making it to become less acidic.

OH, CH_3, NH_2, $O-CH_3$.

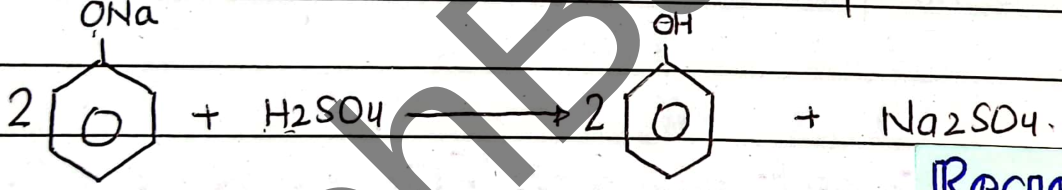
- destabilizes conjugate base

Preparation

1. Sodium Salt of benzene sulphonic acid



Sodium phenoxide.

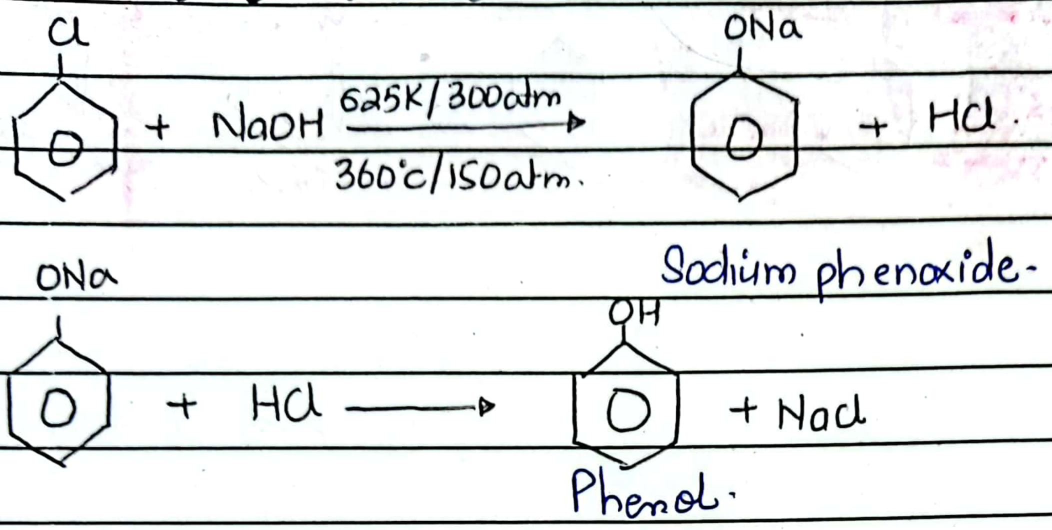


Phenol.

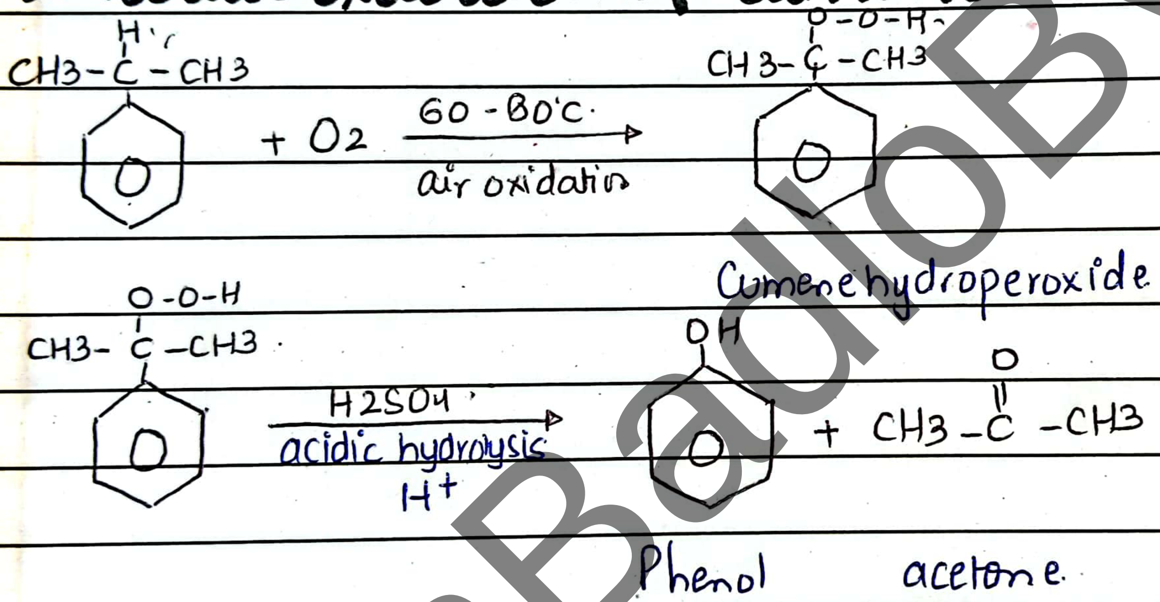
Reactivity

Phenol is more reactive towards electrophillic substitution rxn because of it's nature of ortho-para directing group. That makes availibility of e^- max & thus enhancing capability to react with E^+.

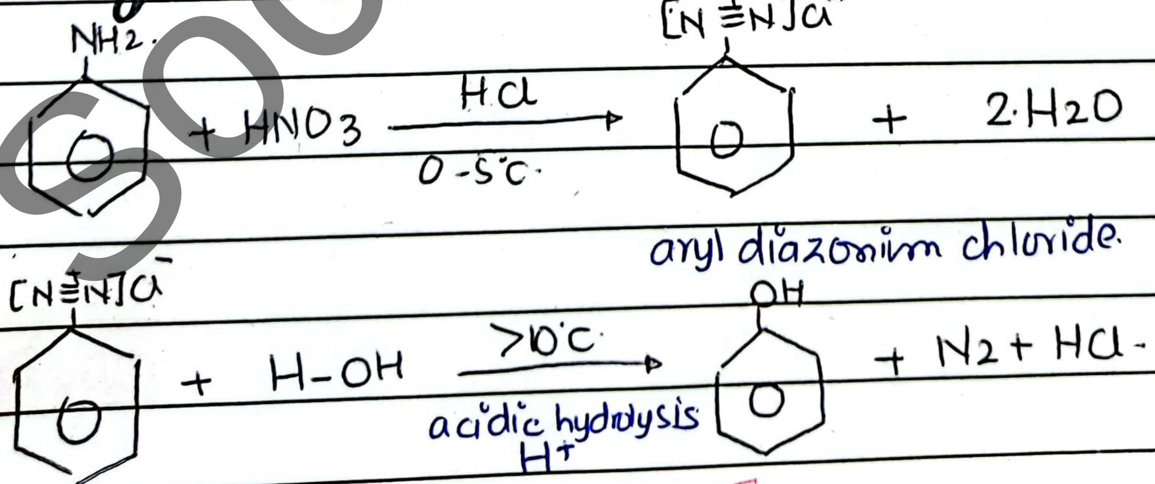
2. Chlorobenzene (Dow's Method)



3. acidic oxidation of cumene



4. aryl diazonium salt (aniline)



13-10-24

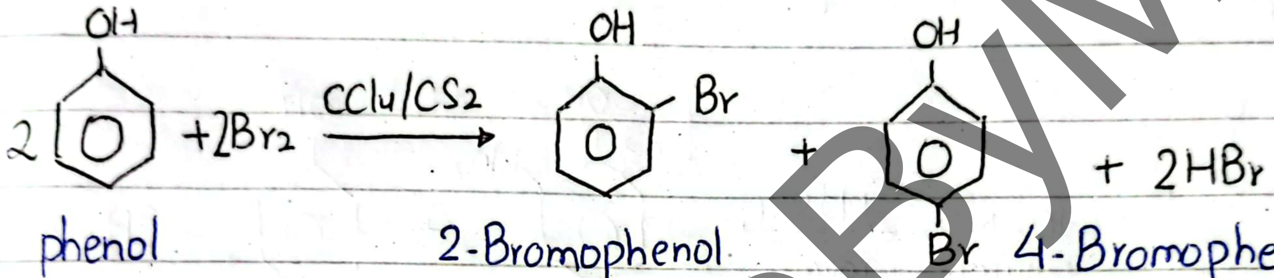
reactions

a) reactions due to benzene ring

1- halogenation

"Replacement of H-atom by halogen"

→ take place in presence of non-polar solvents CCl_4 or CS_2



phenol 2-Bromophenol 4-Bromophenol.

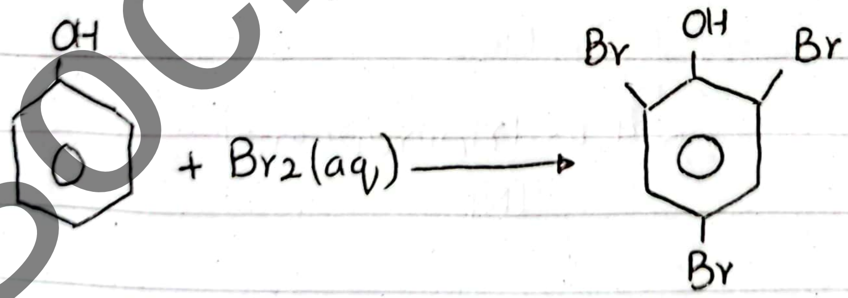
→ Para has more boiling point than ortho due to physical prop.

Para B.P > ortho B.P

→ Para is the major product also because more stability due to more distance b/w 2 bulky group OH & Br.

and

· Phenol on rxn with bromine water, will give us 2,4,6-Tribromophenol / in Presence of polar solvent



2,4,6-Tribromophenol (white ppt)

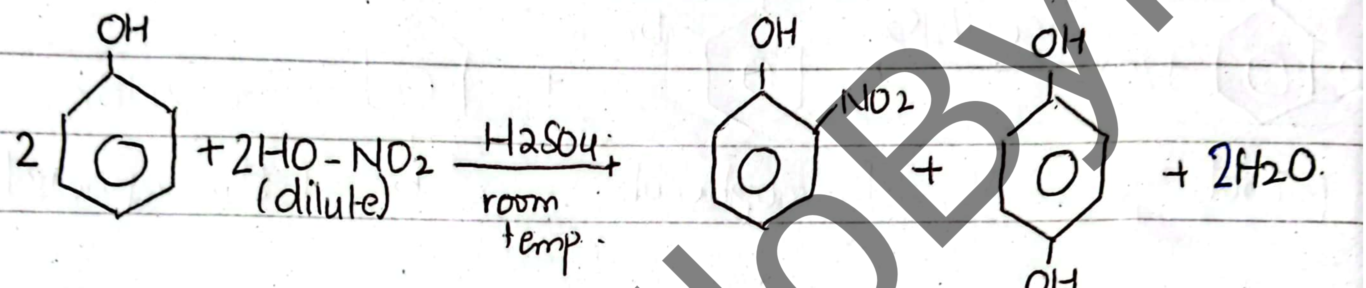
↳ This is identification test of Phenol.

↳ When phenol is reacted with Br_2 water that's brown in color, it gave us white ppt of 2,4,6-Tribromophenol & brown color of Br_2 is disappeared.

2. Nitration

" Replacement of H-atom by nitro group".

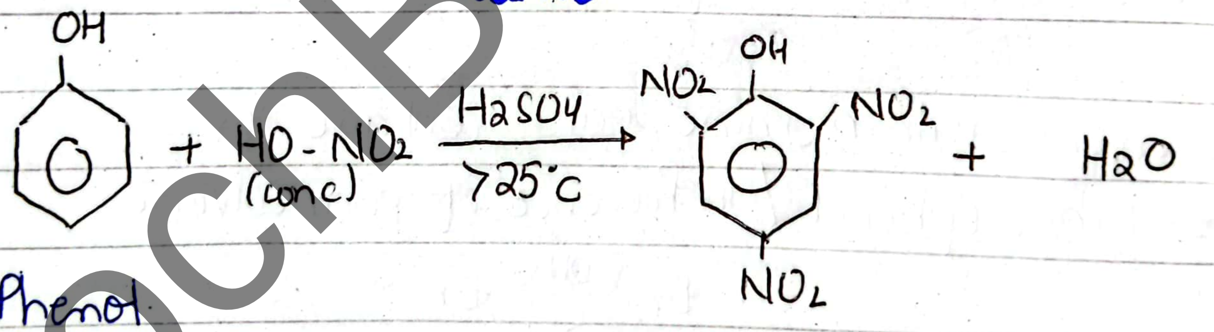
$HNO_3 + H_2SO_4$ [Nitrating mixture]
1 : 1



phenol (ortho) (2-nitrophenol) (Para) (4-nitrophenol)

★ para is major product than ortho.

and



Phenol

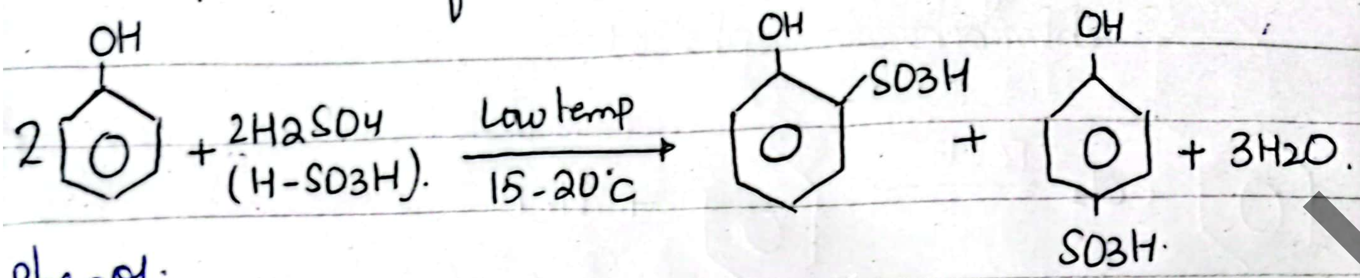
2,4,6-Trinitrophenol
TNP.

Conversion:-

Convert Benzene into Picric acid.

3. Sulphonation

"The replacement of H-atom with Sulphonic grp (SO_3H).



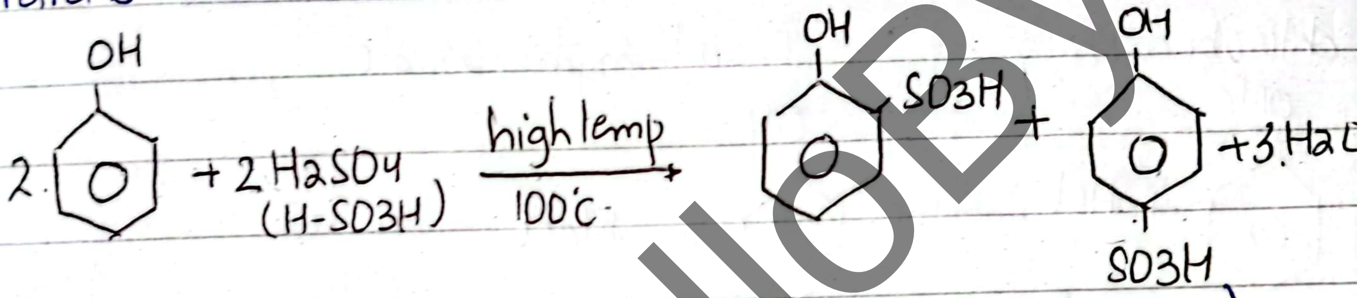
Phenol.

2-Hydroxybenzene sulphonic acid (20°C)

4-Hydroxy benzene sulphonic

Exception:

→ Ortho is more stable at low temp & at high temp (100°C) Para is more stable.

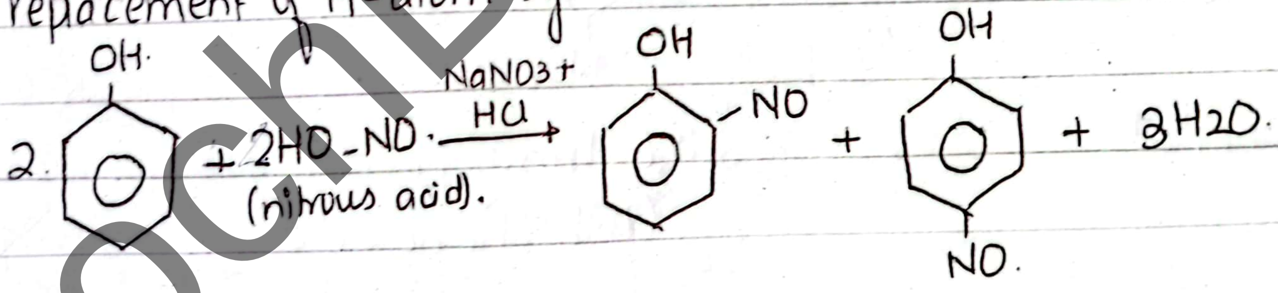


(less) ↳ minor

(Major) ↳ more.

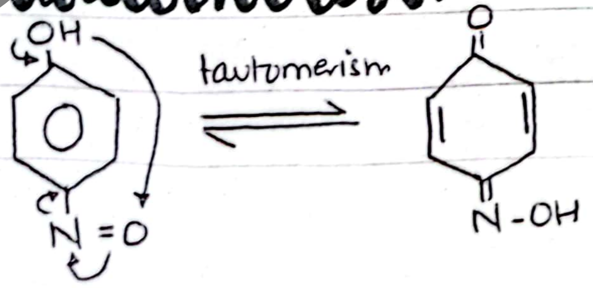
4. Nitrosation

"replacement of H-atom by nitroso"



→ Para is major than ortho.

↳ **tautomerism**

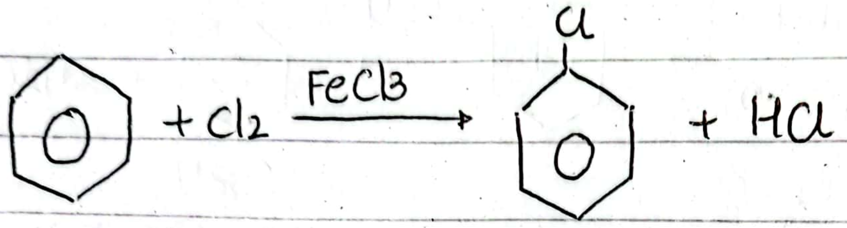


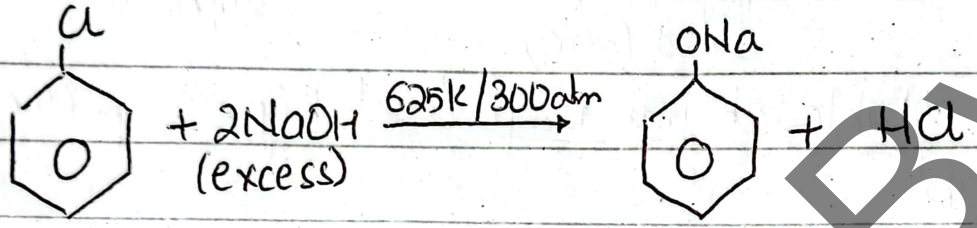
Parabenzoquinone oxime (Yellow crystal).

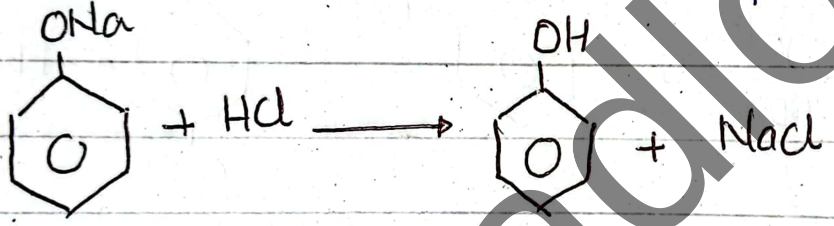
Conversion

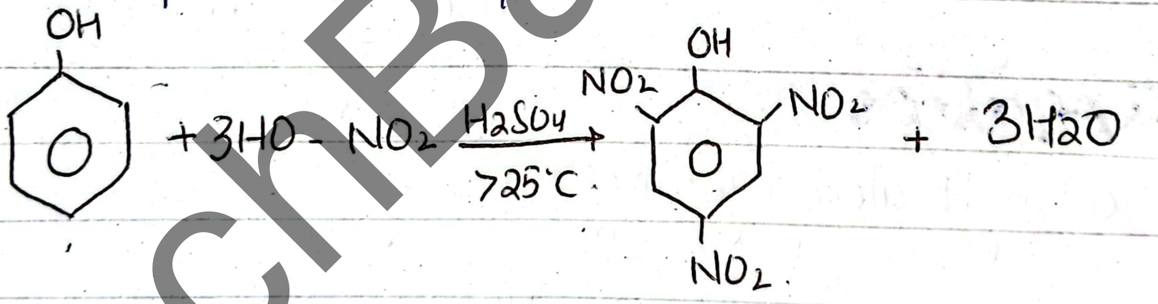
benzene to Picric acid

Benzene + halogenation ⟶ Dow method ⟶ nitration
chlorobenzene phenol





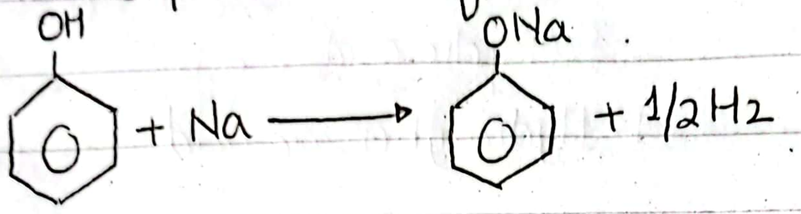




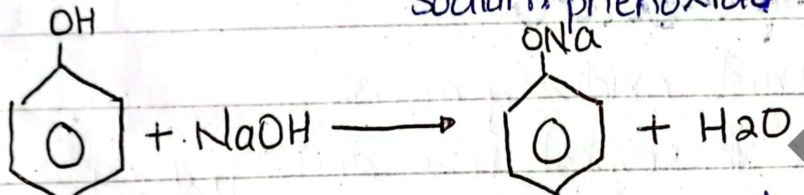
b) Reaction due OH grp (acidic chara of phenol)

reaction with Na or NaOH

Phenol is acidic. So its reaction base or metal will led to the production of Salt.



Sodium phenoxide.



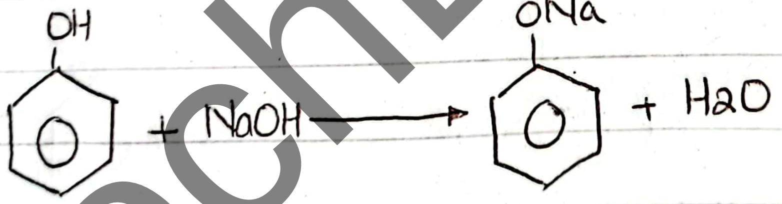
Sodium phenoxide

Phenol is very weak acid, so it doesn't give any color ~~ar~~change on litmus Paper.

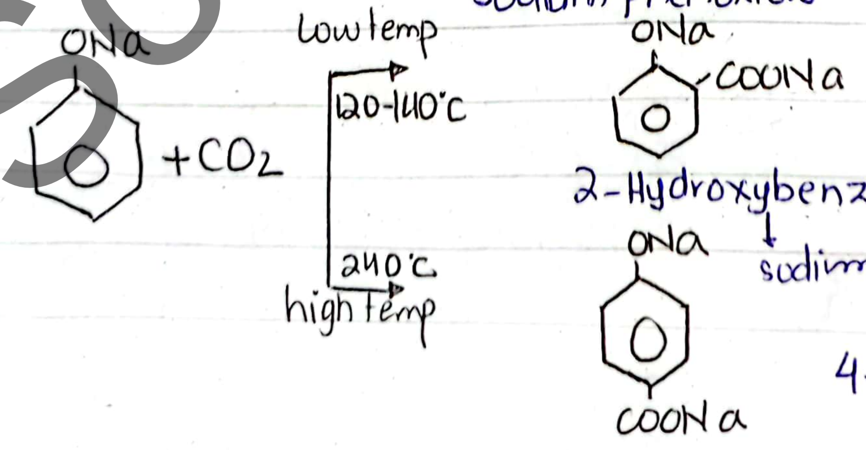
On rxn with CO_3^{-2} or HCO_3^-, it doesn't liberate CO_2.

Carboxylation (Kolbe-Schmitt rxn)

"Reaction of Phenol with CO_2" ⟶ Sodim Salicylate



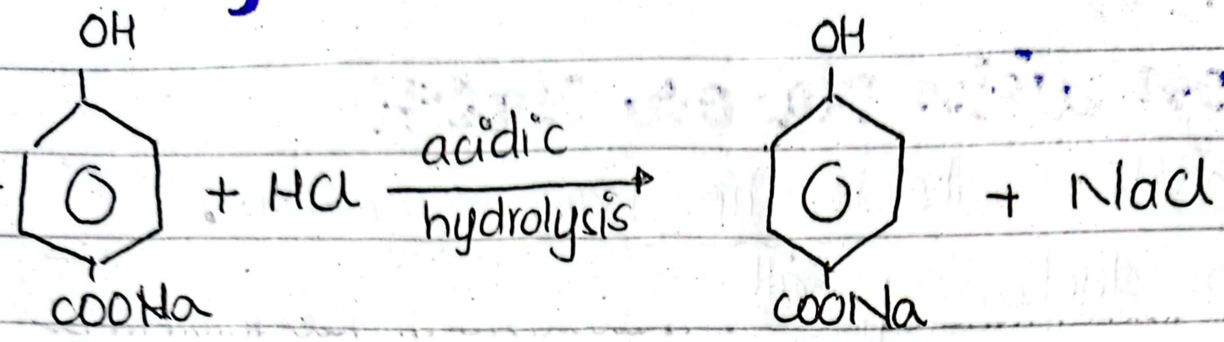
sodium phenoxide..



2-Hydroxybenzoate.
↓
sodim.

4-Hydroxy sodium benzoate.

Salicyclic acid



Sodim Salicylate

Salicyclic acid

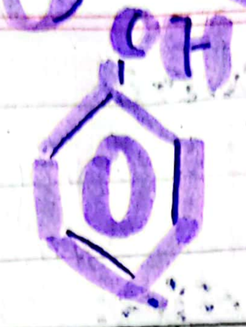
4 - Hydroxybenzoic acid

Oxidation of phenol

phenol is reactive towards oxidizing agent.

Oxidation take place in several steps destroyingring.

diff b/w OH and



alcohols	Phenol
derivates	
hydroxyl derivales of alkane.	derivates of benzene.
replacement of H	
It's a compound in which H-atom is replaced by alky group.	It's a compound in which H-atom is replaced by phenol.
general formula	
R-OH	C_6H_5-OH
physical property	
• Lower alcohols are generally liquid.	Phenol are colorless, crystalline, disliquescent solids.
odour	
They have sweet smell.	They have phenolic smell
taste	
They have burning taste.	They have astringent & medical taste
Solubility	
• Readily soluble in water but decreases in higher alcohol.	Sparingly soluble in water forming pink sol at 25°c but completely soluble at 68.5°c.

structure	
They ~~are~~ don't possess resonating structure.	They possess resonating structure.
reaction	
Reactivity due to breakdown of C–O & O-H bond.	Reactivity due to benzene ring & OH grp.
pka	
pka ≈ 16-20.	pka ≈ 10.

ether

alkoxyalkane or ether (R-O-R).
When oxygen is directly bonded with 2 alkyl groups, the ompound formed is called ether

akoxy ← C-O | C → alkane

If 2 alkyl groups are same symmetrical ether.
If 2 alkyl groups are different unsymmetrical ether.

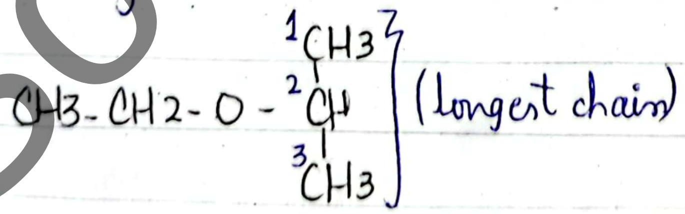
CH_3-O-CH_3 symmetrical ether

$C_6H_5-O-CH_3$ unsymmetrical ether

Nomenclature

CH_3-O-CH_3
Dimethyl ether (C.N).
Methoxymethane (IUPAC)

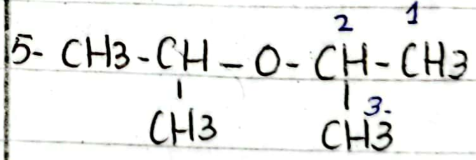
$CH_3-O-CH_2-CH_3$
Ethylmethylether (C.N)
Methoxyethane (IUPAC)



$CH_3-CH_2-O-\overset{2}{C}H(\overset{1}{C}H_3)(\overset{3}{C}H_3)$ (Longest chain)

Ethoxyisopropyl ether (C.N).
2- Ethoxylpropane.

4- $CH_3-CH_2-O-CH_2-CH_3$
Diethylether (C.N).
Ethoxylethane (IUPAC)



5- $CH_3-\underset{CH_3}{CH}-O-\underset{\overset{3}{C}H_3}{\overset{2}{C}H}-\overset{1}{C}H_3$

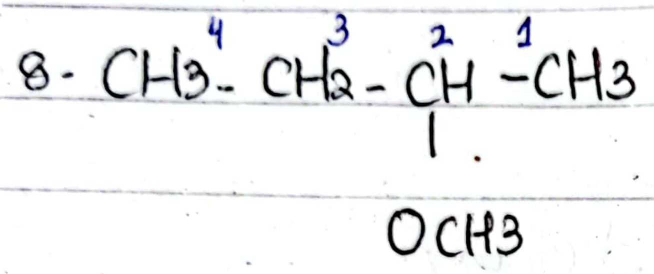
Di iso propylether (C.N
2- isopropoxypropane (IUPA

6- $CH_3-O-C_6H_5$
Methoxyl phenylether (C.N)
(anisole) C.N.
Methoxylbenzene (IUPAC).

7 $C_6H_5-O-C_6H_5$

Diphenylether (C.N).

phenoxylbenzene (IUPAC).

8-


$\overset{4}{CH_3}-\overset{3}{CH_2}-\underset{\overset{|}{OCH_3}}{\overset{2}{CH}}-\overset{1}{CH_3}$

isobutylmethyl ether (C.N).

2- Methoxybutane (IUPAC).

Preparation

i- Williamson Synthesis

) $CH_3-CH_2-OH + Na \longrightarrow CH_3-CH_2-ONa + \frac{1}{2}H_2$

ethanol — Sodium ethoxide

$CH_3-CH_2-ONa + Cl-CH_2-CH_3 \longrightarrow CH_3-CH_2-O-CH_2-CH_3 +$

Sodium ethoxide — ethylchloride — diethylether + NaCl

) $CH_3OH + Na \longrightarrow CH_3-ONa + \frac{1}{2}H_2$

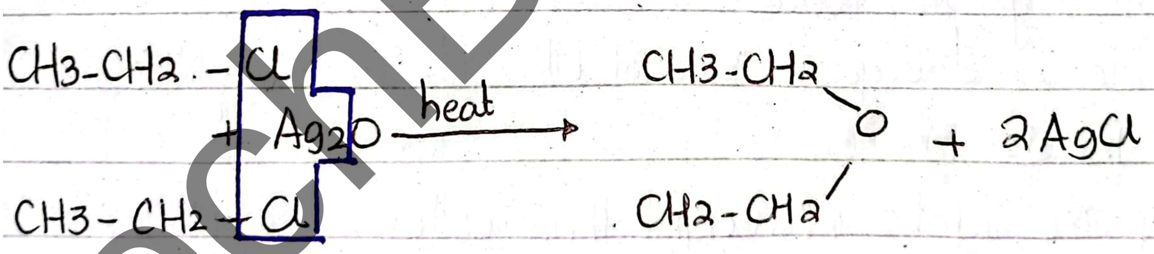
methanol — Sodium methoxide

$CH_3-ONa + Cl-CH_2-CH_3 \longrightarrow CH_3-O-CH_2-CH_3 + NaCl$

Sodium methoxide — ethyl chloride — ethylmethylether.

* Prefered for both symmetrical & Unsymmetrical ether.

Reaction of alkyl halide with dry silver oxide



$$CH_3-CH_2-Cl + Ag_2O + CH_3-CH_2-Cl \xrightarrow{heat} CH_3-CH_2-O-CH_2-CH_2 + 2AgCl$$

*Prefered for symmetrical ether.

Dehydration of alcohol

$CH_3-CH_2-OH + OH-CH_2-CH_3 \xrightarrow[140°C]{H_2SO_4} CH_3-CH_2-O-CH_2-CH_3 + H_2O$

methanol — ethanol — Diethyl ether.

ii- $3CH_3-OH + 3CH_3-CH_2-OH \xrightarrow[140^\circ c]{H_2SO_4 \text{ conc}} CH_3-O-CH_3$ +

Dimethyl ether

$CH_3-O-CH_2-CH_3$ +

ethylmethylether

$CH_3-CH_2-O-CH_2-CH_3$

Diethylether.

Physical Properties

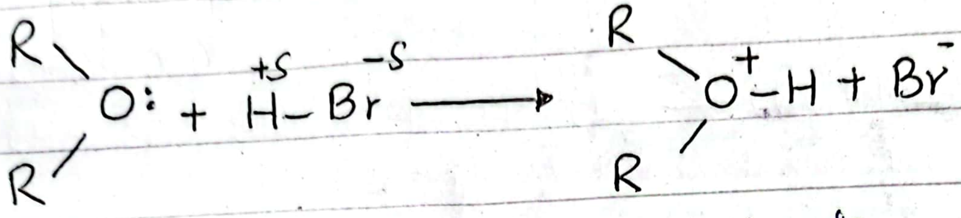
1) Volatile liquids
2) highly inflammable.
3) Lower boiling point
4) Lewis concept considered ether as base.
5) Lower ethers are used as Anesthetics.
6) Used as solvent
7) Slightly soluble in water because they form weak H- bonding with water.
8) Soluble in Inorganic solvent Like H_2SO_4, Liq NH_3, H_2O, HCl, etc.
9) They are lighter in weight than water.

Chemical Properties

1) Inert towards Acid & bases.
2) Reactive with oxidizing & reducing agents.
3) Not reactive with Na metal.

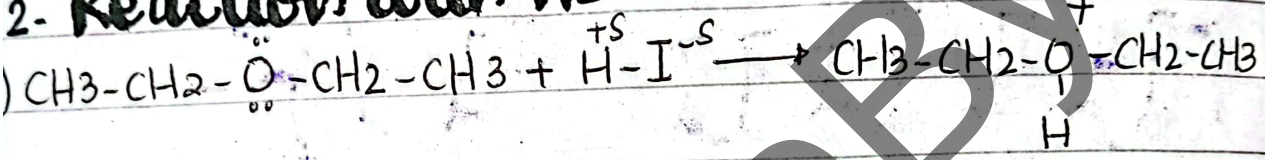
reaction

1- Reaction with HBr



Oxonium ion

2- Reaction with HI



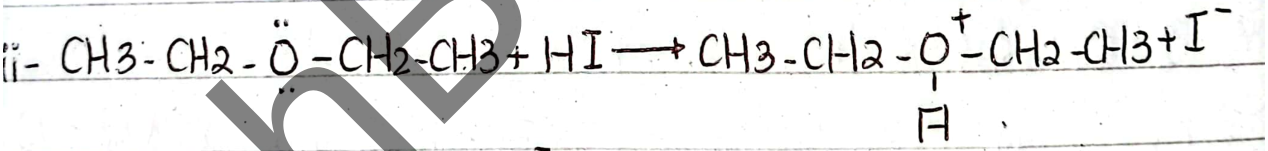
$$CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_2-CH_3 + \overset{+\delta}{H}-\overset{-\delta}{I} \longrightarrow CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3$$

Oxonium ion $+ I^-$

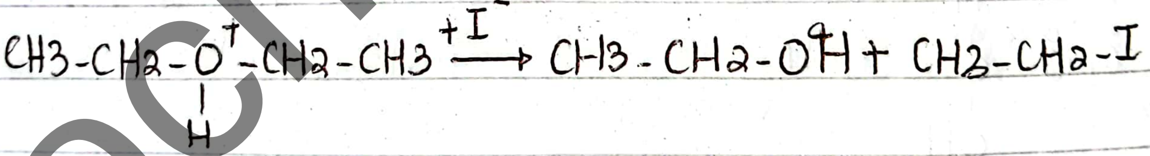
$$CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 + I^- \longrightarrow CH_3-CH_2-OH + CH_3-CH_2-I$$

ethanol ethyl Iodide

or



$$ii-\ CH_3-CH_2-\ddot{O}-CH_2-CH_3 + HI \longrightarrow CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 + I^-$$



$$CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 \xrightarrow{+I^-} CH_3-CH_2-OH + CH_2-CH_2-I$$

↓ same as above, mistakely written.

Reaction with PCl_5

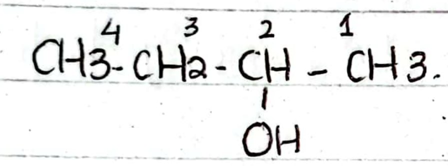
$CH_3-CH_2-O-CH_2-CH_3 + \underset{(hot)}{PCl_5} \longrightarrow 2CH_3-CH_2-Cl + POCl_3$

phosphorus oxy chloride

reactive review Q18

Question 3

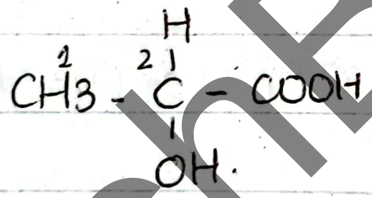
2.

i) 

$\overset{4}{C}H_3-\overset{3}{C}H_2-\underset{OH}{\overset{2}{C}H}-\overset{1}{C}H_3$

Sec-butylalcohol

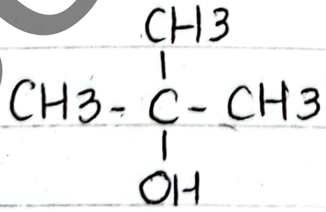
2-Butanol

ii) 

$\overset{1}{C}H_3-\underset{OH}{\overset{H}{\overset{2}{C}}}-COOH$

2-Hydroxypropanoic acid

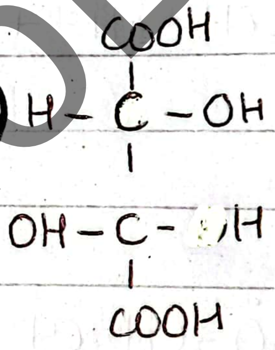
Lactic acid

iii) 

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

ter-butylalcohol

2-Methyl-2-Propanol

iv) 

$$\begin{array}{c} COOH \\ | \\ H-C-OH \\ | \\ OH-C-OH \\ | \\ COOH \end{array}$$

2,3-Dihydroxybutanedioicacid

Tartaric acid

7-

- Reason

ethyl alcohol

The ethyl alcohol has strong intermolecular force of interaction due to high electronegativity difference. This led to high boiling point & keeps it liq at 25°C.

ethyl chloride

The ethyl achloride has weak dipole-dipole interactions and Vander Waals forces leading to weak structure. laking boiling point lower & keep it gas at 25°C

i- Reason

he reactions pathway changes because temperature affects the availability of energy to break bonds & orm different bonds.

At low temp (140°C) there's enough energy to form diethyl ether.

at high temp (180°C) there's additional energy that favours the elimination rxns.

ii- Reason

water It's boiling point about 100°C. Due to extensive and strong H-bonding, making B.P quite higher.

ethanol It's boiling point about 78.37°C. Has H-bonding, they aren't as strong as those because in water -OH grp is only part of

diethylether boiling point is about (34.6°c). lack hydrogen bonding & relies mainly on Van der Waals forces, resulting in quite lower B.P.

SLO

Q. Why lower alcohols are more soluble than higher alcohols?

Lower alcohols are more soluble than higher alcohols because of polarity of OH group decreases. The OH is a highly electronegative compound, but as R group increase it decreases its polarity.

$\boxed{\text{Reactivity} \propto \text{Solubility}}$

Q. How will you distinguish between 1 propanol, 2 propanol & 2-Methyl-2 propanal?

We can distinguish by "lucas test".

1- 1-Propanol:-

It's primary alcohol, when reacted with HCl it will form an insoluble oil layer after heating.

2- 2-Propanal :-

It's secondary alcohol, when reacted with HCl it forms an insoluble oil layer after nearly 5-10min.

.2-Methyl-2-Propanol:

It's tertiary alcohol, when reacted with HCl it will immediately form oil layer.

. When carboxylic acid is more stable than phenol?

Carboxylate ion is more stable than phenoxide because negative charge is more delocalized in COOH case than C_6H_5-OH case such that t lead to the more stability.

. Why nitrophenol is more acidic than phenol?

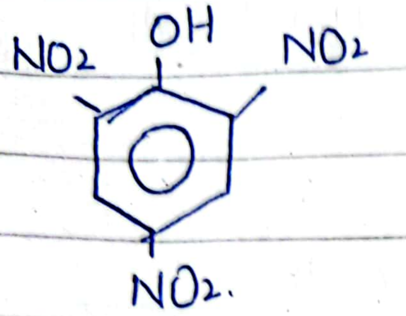
Nitrophenol is more acidic than phenol because NO_2 is meta-directing group, that with-draws he electrons leading to increase in acidity.

. Why are thiols more acidic than alcohols?

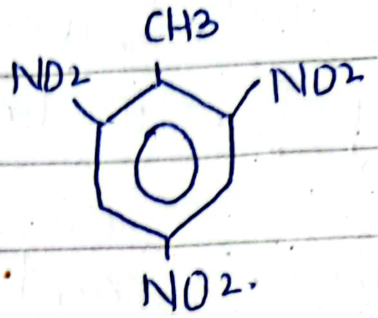
$$\boxed{PKa \propto \frac{1}{acidity}}$$

ka value of thiol is Smaller (≈ 10) than PKa value of alcohol (≈ 16-20). Therefore acidity of thiol is nore than alcohol.

Q Difference b/w TNT & TNP.



&



2,4,6-Trinitrophenol
Picric acid.

2,4,6-Trinitrotoluene

Q. Nitration of nitrobenzene occurs at 50-55°C while nitration of phenol occurs at room temp.

Phenol is more reactive towards electrophillic substitution reaction than benzene, -OH group in phenol is ortho-para directing group that donates electrons to the benzene ring making it e^--rich at o & p positions. Incoming electrophile is more likely to attack here.

Exercise

1: Select the right answer from the choices given with each question.

i. Which compound shows hydrogen bonding?

a. C_2H_6 b. C_2H_5Cl c. CH_3-O-CH_3 [✓ d. C_2H_5OH]

ii. According to Lewis concept ethers behave as

a. Acid [✓ b. Base] c. Acid as well as base d. None of them

iii. Ethanol can be converted into ethanoic acid by

a: Hydrogenation b: Hydration [✓ c: Oxidation] d: Fermentation

iv. Williamsons synthesis of ethers is superior to alcohols because it makes

a. Symmetrical ethers b. Asymmetrical ethers

c. Ether at room temperature [✓ d. Both symmetrical and asymmetrical Ethers]

v. Which one of the following compounds does not contain carboxylic group?

a. Acetic acid b. Formic acid c. Benzoic acid [✓ d. Picric acid]

vi. Hydrogen bonding is maximum in

a. Diethyl ether [✓ b. Ethanol] c. Ethanal d. Triethyl amine

vii. Which of the following compounds have no attraction at all with water?

[✓ a.] C_6H_6 b. C_2H_5OH ✓ c. $CH_3CH_2CH_2OH$ d. CH_3-O-CH_3

viii. Phenols are more acidic than alcohols. Which statement is correct?

a. Phenol turns blue litmus paper red

b. Alcohol liberates CO_2 with carbonate solution

[✓ c.] Phenoxide ion is stabilized due to resonance

d. Alkoxide ion is stabilized due to resonance

ix. Carbolic acid is treated with dilute nitric acid at 25 ºC, and the product is

a. o-nitrophenol b. p-nitrophenol c. m-nitrophenol [✓ d.] Both a and b

x. Oxonium ion is formed when

a. Ethanol reacts with Na metal b. Phenol reacts NaOH solution

[✓ c.] Ether is treated with HI d. Ethanol is treated with aq. NaOH and iodine

xi. 2,4,6-Trinitrophenol is commercially called as

a. TNT [✓ b.] Picric acid c. Carbolic acid d. Fumeric acid

2: Answers the following questions briefly.