Alcohols, Phenols, and Ethers....

Introduction..

Hydroxyl derivatives of hydrocarbons are alcohols. Alcohols are formed when a hydrogen atom in a hydrocarbon is replaced by -OH group. Functional group in alcohols is -OH groups.

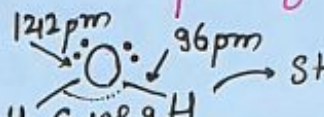
Alcohols..

#Classification :—

- Alcohols are classified as mono, di, tri or polyhydric compounds depending on whether they contain one, two or three or many -OH groups.

#Structure :—

- In alcohols, oxygen atom of the -OH group is attached to sp^3 hybridised carbon by sigma bond.
- It is due to repulsion between unshared pair of electrons of oxygen.

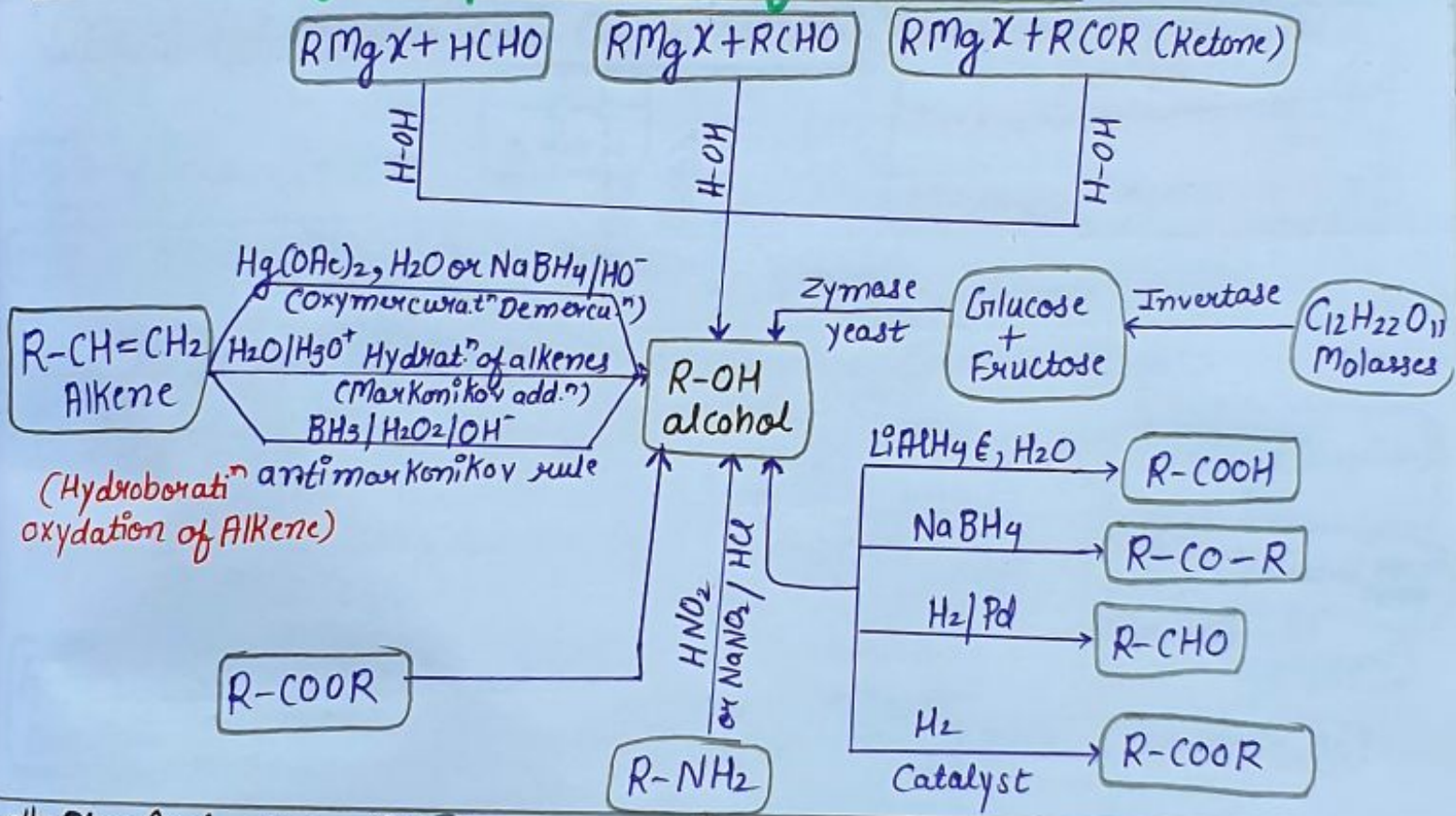


Structure of Methanol

#Isomerism :—

- Alcohols may exhibit chain, positional and functional isomerism.
- Functional isomers of alcohols are ethers.

Methods Of Preparation Of Alcohols...



#Physical properties

- In alcohols, boiling points decreases with increase of branching in carbon chain due to decrease in Van der Waals forces with decrease in surface area.

eg- n-Butyl alcohol > Isobutyl alcohol > tertiary butyl alcohol.

- Solubility of alcohol in water decreases with increase in size of alkyl group.

Chemical Reactions → Alcohols can act as nucleophiles and protonated alcohols act as electrophiles.

Acidity of Alcohols → alcohols are acidic in nature. Alcohol behave as Bronsted acids. With bases stronger than its alkaloide.

$$\underset{\text{acid}}{R-O-H} + :\underset{\text{Base}}{B^-} \longrightarrow \underset{\text{Conj. acid}}{B-H} + \underset{\text{conj. base.}}{R-\ddot{O}:}$$

- Acidic character of alcohols is due to polar nature of O-H bond.
- Alkyl groups, being electron releasing groups increases electron density on oxygen tending to decrease the polarity of O-H bond. So acid strength of alcohols decreases.

$$R-CH_2OH > \begin{matrix} R \\ R \end{matrix}\!\!>CHOH >> \begin{matrix} R \\ R \\ R \end{matrix}\!\!>C-OH$$

- Acidic nature of alcohols is less than water due to electron releasing alkyl group.

$$\underset{\text{Base}}{R-O^-} + \underset{\text{acid}}{H-O-H} \longrightarrow \underset{\text{conj. a.}}{R-O-H} + \underset{\text{conj. base.}}{OH^-}$$

- Action with HX

$$ROH + HX \xrightarrow[ZnCl_2]{\text{anhy.}} RX + H_2O$$

Order of reactivity: HI > HBr > HCl > HF

3° Alcohol > 2° alcohol > 1° alcohol.

- A mixture of Conc. HCl and anhydrous $ZnCl_2$ is called Lucas reagent.

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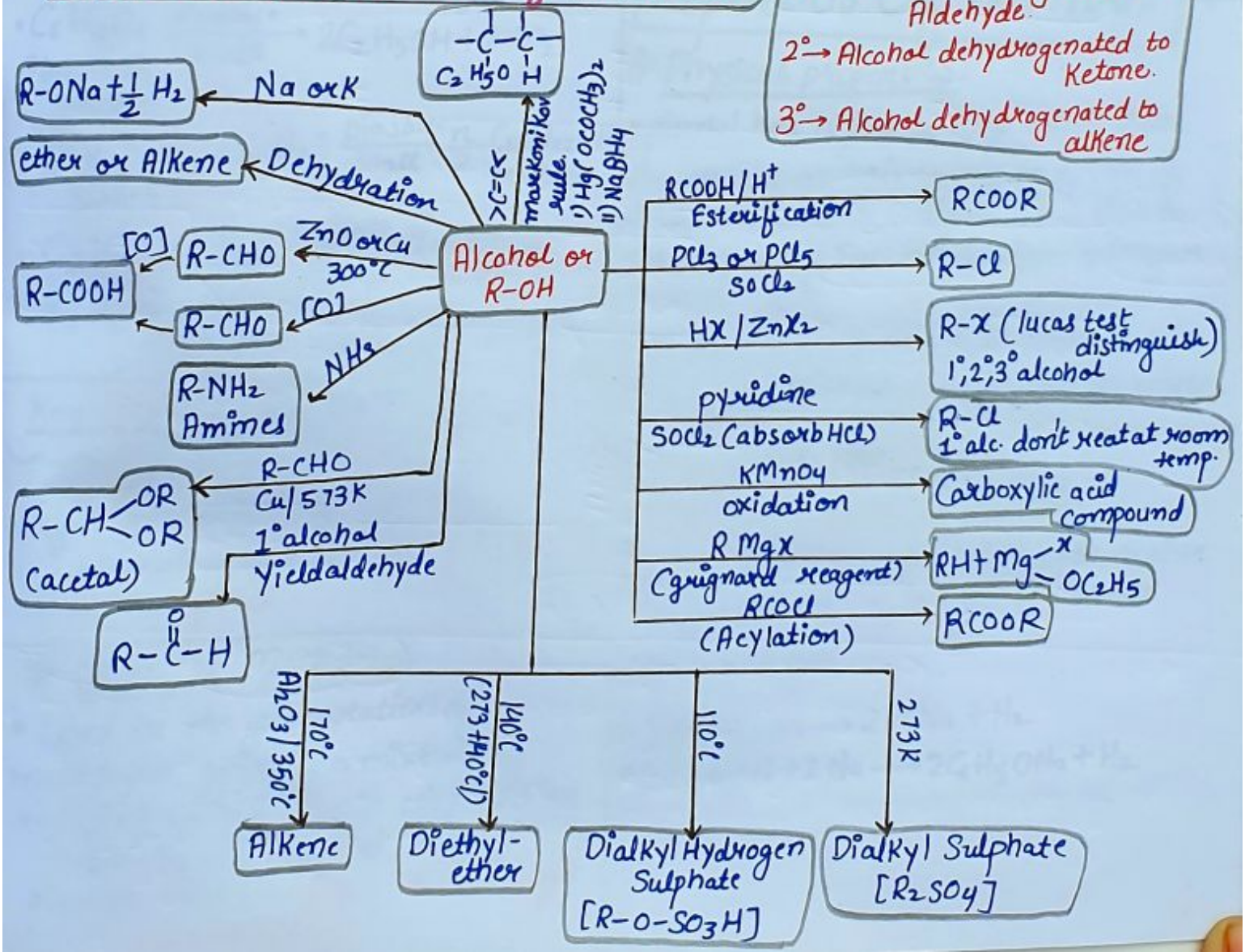
Chemical Reactions Of Alcohol...

1° → Alcohol dehydrogenated to Aldehyde.
2° → Alcohol dehydrogenated to Ketone.
3° → Alcohol dehydrogenated to alkene



Hydroboration Reaction :-

$$CH_3CH_2CH=CH_2 \xrightarrow[H_2O,\ H_2O_2,\ OH^-]{B_2H_6} CH_3CH_2CH_2OH$$

Some Commercially Imp. Alcohols Reactions..

Methanol.

- Known as wood spirit.

Preparation.

$$CO_2 + 2H_2 \xrightarrow[200-300\,atm,\ 573-673K]{ZnO-CrO_3} CH_3OH$$

Ethanol

↳ preparation

- $C_{12}H_{22}O_{11} + H_2O \xrightarrow[Yeast]{Invertase} C_6H_{12}O_6$ (glucose) $+ C_6H_{12}O_6$ (fructose)
- $C_6H_{12}O_6$ (Glucose or fructose) $\xrightarrow[Yeast]{Zymase} 2C_2H_5OH + 2CO_2$.
- $(C_6H_{10}O_5)n$ (starch) $+ \frac{n}{2}H_2O \xrightarrow[malt]{Diastase} \frac{n}{2}C_{12}H_{22}O_{11}$ (maltose)
- $C_{12}H_{22}O_{11} + H_2O \xrightarrow[yeast]{Maltase} 2C_6H_{12}O_6$ (glucose)
- $C_6H_{12}O_6 \xrightarrow[yeast]{zymase} 2C_2H_5OH + 2CO_2$ (ethanol).

Key Note → The industrial alcohol or rectified spirit is denatured to make it unfit for drinking. The denatured alcohol is also called methylated spirit.

Uses Of Methanol.

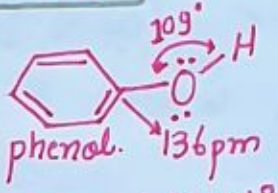
- Used in the preparation of methylated spirit, a mixture of rectified spirit (95.6% ethyl alcohol + 4.4% water) and methyl alcohol making ethyl alcohol unfit for drinking.

Uses of ethanol :-

- A preservative for biological specimens, an antifreeze for automobile radiators, a fuel in spirit lamps, stoves, a petrol substitute known as power alcohol.

Phenols.

Structure.



- The C-O bond length is slightly less than in methanol. This is due to partial bond double character on account of conjugation of unshared electron pair of oxygen with the aromatic ring.

Properties Of Phenol..

Physical properties.

- phenol has higher boiling point than the arenes or haloarenes or ethers of same molecular weight. It is due to formation of intermolecular hydrogen bond.
- As the hydrocarbon part increases in size, and mass, the solubility decreases.

Chemical Reactions.

(1) Acidic nature of phenol.

- Alcohols and phenols react with active metals like Na, K, Al etc.. to liberate hydrogen gas.

* $2ROH + 2Na \rightarrow 2RONa + H_2$
* $2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$

- Electron releasing groups like alkyl groups increase the electron density on oxygen and decrease the polarity of O-H bond. This decreases the acidic strength.

* The order of acidic strength is :-

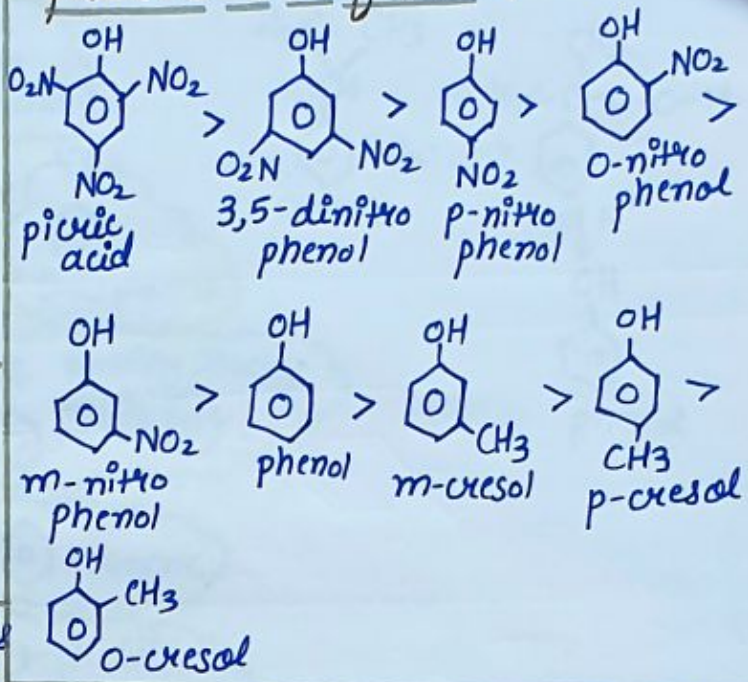
$H_2O > RCH_2OH > R_2CHOH > R_3COH$

Relative acid strength.

- Carboxylic acid > Carbonic acid > phenol > Methyl alcohol > Water > other alcohols.

- The reactions of phenol with metals as well as NaOH indicate that phenol is relatively more acidic than alcohols and also water.
- The sp^2 carbon attached to 'O' being more electronegative than carbon of alcohols, it decreases the electron density on oxygen. Because of this, oxygen develops still more electron seeking character and releases proton by taking the shared pair of electron with it.
- The acidic nature of phenol can also be explained on basis of resonance Stabilization of phenoxide ion.
- Acidic strength increases with the decrease of pK_a values.

* Order of acidic strength of phenols is as follows :-



- Greater the pK_a value, weaker the acid.
- Electron releasing groups like $-CH_3$, $-C_2H_5$ etc.. decrease the acidic strength of phenol and electron withdrawing group increases acidic strength of phenol.

Key Note → Ortho and para isomers can be separated by steam distillation.

- O-nitrophenol is steam volatile due to intramolecular
- p-nitrophenol is less volatile due to intermolecular hydrogen bond

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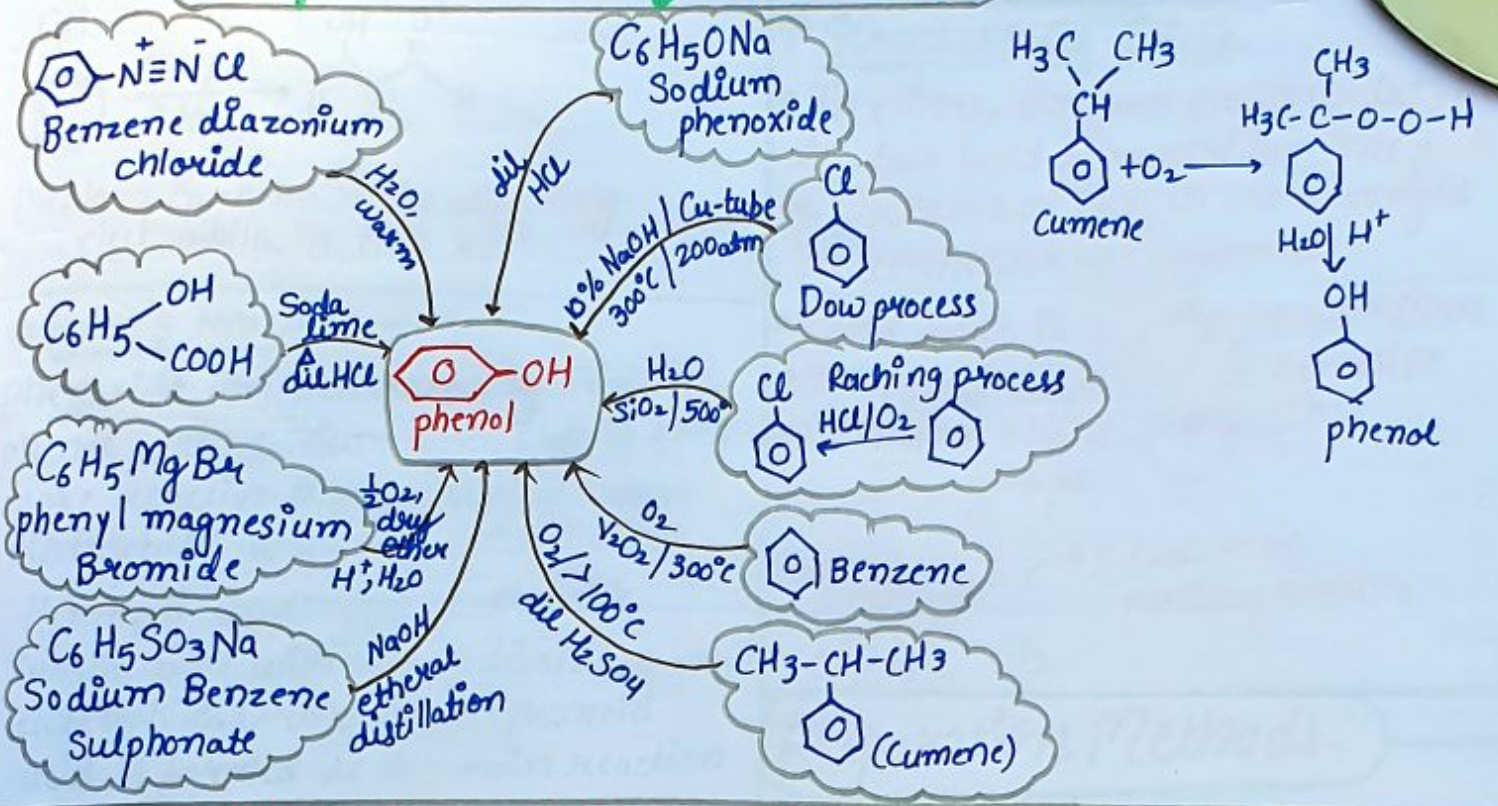
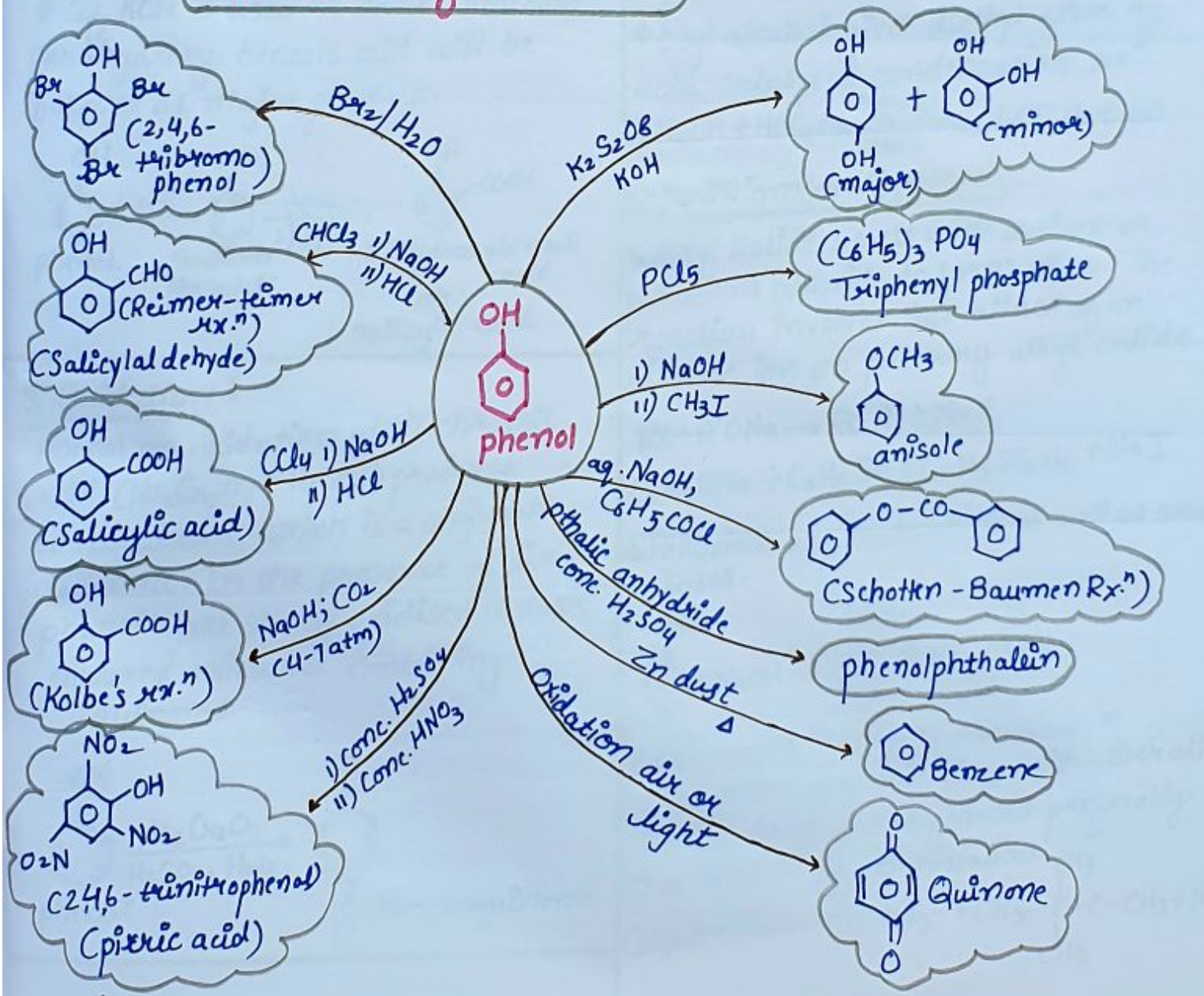
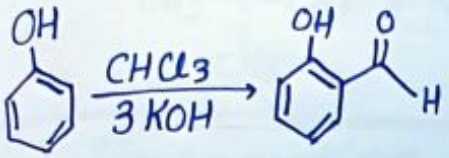
Preparation Of Phenol



Reaction Of Phenol..



Reimer-Tiemann Reaction →



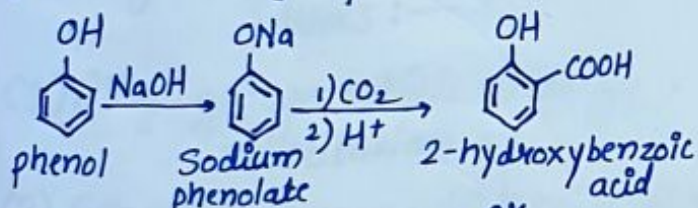
Dichloro carbene is the attacking electrophile in this rx.n

Kolbe's reaction →

phenoxide ion generated by treating phenol with sodium hydroxide is even more reactive than phenol towards electrophilic aromatic substitution.

Hence, it undergoes electrophilic substitution with carbon dioxide, a weak electrophile. Ortho hydroxybenzoid acid is formed as the main reaction product.

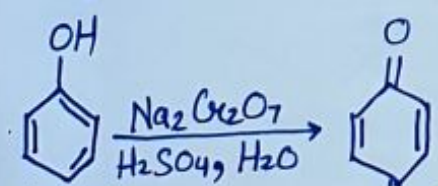
- If KOH is used in Kolbe's reaction parahydroxy benzoic acid will be formed as major product.



phenol — Sodium phenolate — 2-hydroxybenzoic acid or Salicylic acid.

Oxidation :—

phenol on oxidation with chromic acid ($Na_2Cr_2O_7 + H_2SO_4$) produces benzoquinone, which is a conjugate diketone. In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.



phenol — Benzoquinone

Ethers...

Structure Of Ether.

- In ethers, the four electronpairs, i.e. the two bond pairs and two lone pairs of electrons on oxygen are arranged in tetrahedral arrangement.
- Bond angle is slightly greater than tetrahedral angle due to repulsive interaction b/w 2 bulky alkyl (-R) groups.

→ Structure of methoxymethane

Preparation Methods..

(1) By dehydration of alcohols.

- Etyl alcohol gives diethyl ether by acid-catalysed condensation rx.n

$$C_2H_5OH + HOC_2H_5 \xrightarrow[140^\circ C]{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

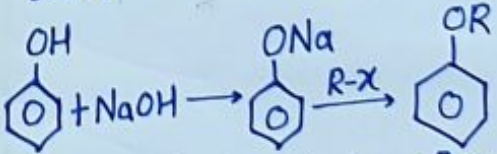
(2) Williamson Synthesis.

- Alkyl halide reacts with sodium or potassium alkoxide to form ether. The reaction involves S_N2 attack of an alkoxide ion on primary alkyl halide.

$$RX + R'ONa \rightarrow ROR' + NaX$$

$$C_2H_5ONa + C_2H_5I \rightarrow C_2H_5OC_2H_5 + NaI.$$

- Alkoxides are nucleophiles as well as strong bases.



Alkyl halide has to be primary in Williamson synthesis bcoz with other alkyl halides alkenes are formed preferably as a result of elimination.

$$CH_3Br + NaO-C(CH_3)_3 \rightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{O}}}}-C-CH_3 + NaBr$$

$(CH_3)_3C-Br + CH_3ONa \rightarrow CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + NaBr$

$CH_3CH_2OCH_2CH_3 \xrightarrow[\text{sunlight}]{Cl_2} C_2Cl_5-O-C_2Cl_5$

(perchloro diethyl ether)

.. Properties ..

Physical properties.

- Ethers are slightly soluble in water and readily soluble in organic solvents due to lack of H-bonding. Boiling point of Diethyl ether is less than its functional isomer butyl alcohol (C_4H_9OH).

Chemical Reactions :—

- Ethers are less reactive than alcohols due to non-availability of active hydrogen.
- Rx.ⁿ of ether are classified into 3 types :—

(1) Alkyl groups which undergo substitution rx.ⁿ.

(2) Ethereal oxygen which co-ordinates with electron deficient molecules like Lewis-acid.

(3) Carbon-Oxygen bond which shows some cleavage reaction.

(1) Reactions of alkyl group.

- **Halogenation →**

Diethyl ether reacts with chlorine or bromine to form halogen substituted ethers. Hydrogens at α carbon atoms are easily substituted in the dark condition.

$CH_3CH_2OCH_2CH_3 \xrightarrow[dark]{Cl_2} CH_3-\overset{\alpha}{C}H(Cl)-\overset{\alpha'}{O}-CH(Cl)-CH_3$

(α-α' dichloro diethyl ether)

(2) Reactions of ethereal oxygen.

$C_2H_5-O-C_2H_5 + (O) \rightarrow C_2H_5-\underset{\underset{O}{\downarrow}}{O}-C_2H_5$

(peroxide)

- **Formation of oxonium Salts :—**

$C_2H_5-O-C_2H_5 + HBr \rightarrow \left[C_2H_5-\overset{+}{\underset{\underset{H}{\downarrow}}{O}}-C_2H_5\right] Br^-$

Diethyl oxonium bromide.

$C_2H_5-O-C_2H_5 + H_2SO_4 \rightarrow \left[C_2H_5-\overset{+}{\underset{\underset{H}{\downarrow}}{O}}-C_2H_5\right] HSO_4^-$

Diethyl oxonium hydrogen sulphate.

(3) Reactions involving cleavage of C–O bond. →

(i) Action of sulphuric acid.

$C_2H_5-O-C_2H_5 + H_2SO_4(conc) \xrightarrow{\Delta,\ 110^\circ C} C_2H_5OH + C_2H_5HSO_4.$

(ii) Action of HX.

$R-OR + HX \rightarrow RX + ROH$

$ROH + HX \rightarrow RX + H_2O$

- In the hot condition with excess of HI →

$C_2H_5-O-C_2H_5 + 2HI \xrightarrow{\Delta} 2C_2H_5I + H_2O$

- Here the cleavage is at alkyl oxygen due to low reactivity of aryl oxygen bond. In the cleavage of mixed ethers lower alkyl group forms alkyl iodide.

NEET SLAYER

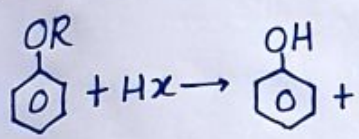
- **Action of HX :-**

$R-OR + HX \rightarrow RX + ROH$

- If 3° alkyl group is present it forms tertiary halide as major product.

$(CH_3)_3-C-OCH_3 + HI \rightarrow CH_3OH + (CH_3)_3CI$

$CH_3-OC_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$



Alkyl aryl ethers are cleaved at the alkyl-oxygen bond due to more stable aryl-oxygen bond.

- **Hydrolysis :-**

$C_2H_5-O-C_2H_5 + H_2O \rightarrow 2C_2H_5OH$.
(Steam)

- **Action of PCl_5 :-**

$C_2H_5-O-C_2H_5 + PCl_5 \rightarrow 2C_2H_5Cl + POCl_3$

- **Action of acetyl chloride :-**

$C_2H_5-O-C_2H_5 + CH_3COCl \xrightarrow{AlCl_3}$

$C_2H_5Cl + CH_3COOC_2H_5$

$C_2H_5-O-C_2H_5 + (CH_3CO)_2O \xrightarrow{ZnCl_2}$

$2CH_3COOC_2H_5$

- **Oxidation :-**

$C_2H_5OC_2H_5 + (O) \xrightarrow{\text{acid. } K_2Cr_2O_7} 2CH_3CHO$

$\xrightarrow{\text{acid } K_2Cr_2O_7} 2CH_3COOH$.

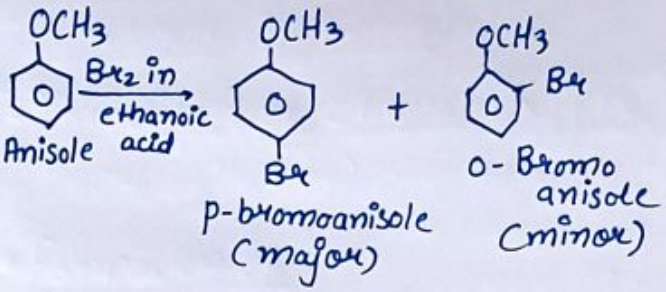
- **Dehydration :-**

$C_2H_5OC_2H_5 \xrightarrow[360°C]{Al_2O_3} 2CH_2=CH_2 + H_2O$

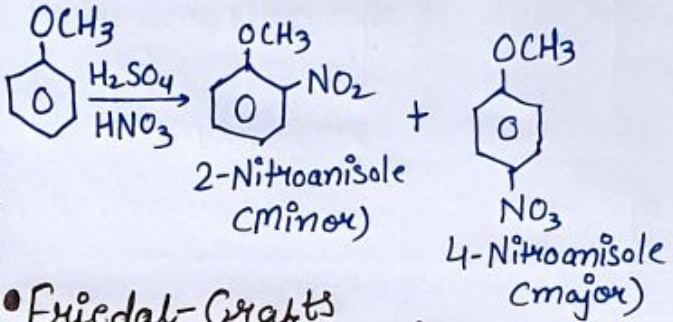
Electrophilic aromatic Substitution on Anisole :-

- **Halogenation →**
- phenyl alkyl ethers undergo usual halogenation in benzene ring. It is due to activation of benzene ring by the methoxy group.

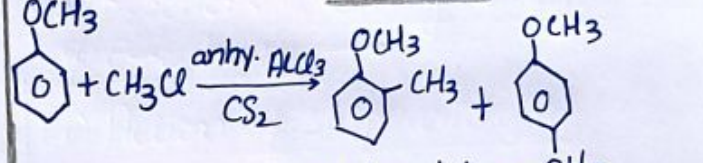
Para isomer obtained in 90% yield.



- **Nitration :→**



- **Friedal-Crafts reaction :-**



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Unlock Your Potential

Slay. ♡

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