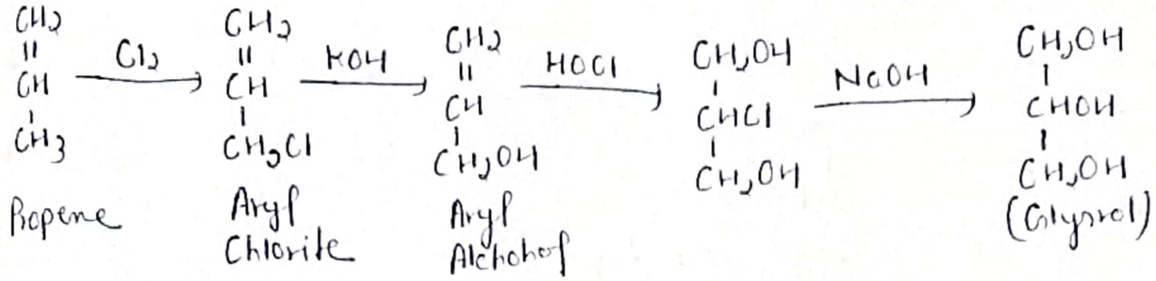
Q:- Methods for Synthesis of Glysrol -

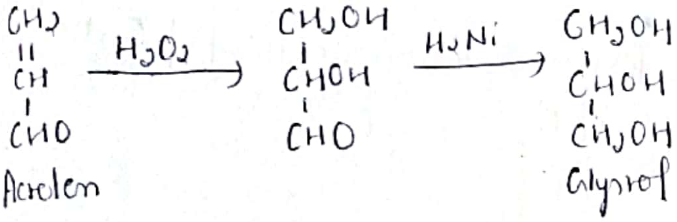
(i) from Propene (Cl_2, KOH, HOCl, NaOH)
(ii) from Acrolen (H_2O_2, H_2Ni)
(iii) from Soponificafian (3NaOH)

(i) from Propene -



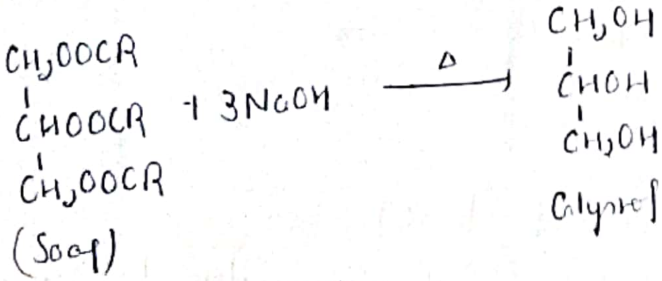
$$\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_3\\ \text{Propene}\end{array}\xrightarrow{Cl_2}\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_2Cl\\ \text{Aryl Chlorite}\end{array}\xrightarrow{KOH}\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_2OH\\ \text{Aryl Alchohol}\end{array}\xrightarrow{HOCl}\begin{array}{c}CH_2OH\\ |\\ CHCl\\ |\\ CH_2OH\end{array}\xrightarrow{NaOH}\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{(Glysrol)}\end{array}$$

(ii) from Acrolen -



$$\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CHO\\ \text{Acrolen}\end{array}\xrightarrow{H_2O_2}\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CHO\end{array}\xrightarrow{H_2Ni}\begin{array}{c}CH_2OH\\ |\\ CHOH\\ CH_2OH\\ \text{Glysrol}\end{array}$$

(iii) from Soponificafian -

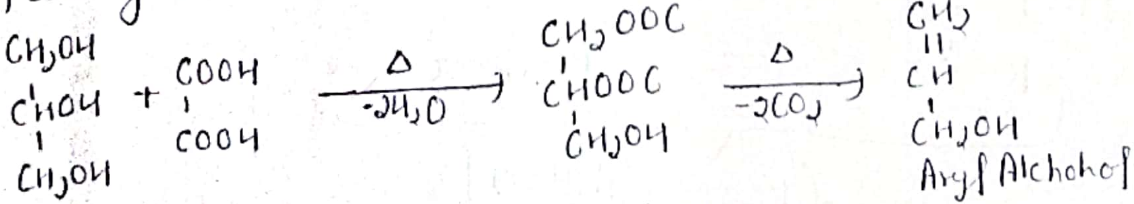


$$\begin{array}{c}CH_2OOCR\\ |\\ CHOOCR\\ |\\ CH_2OOCR\\ \text{(Soap)}\end{array}+3NaOH\xrightarrow{\Delta}\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glysrol}\end{array}$$

Q.II - Glysrol Reacts with-

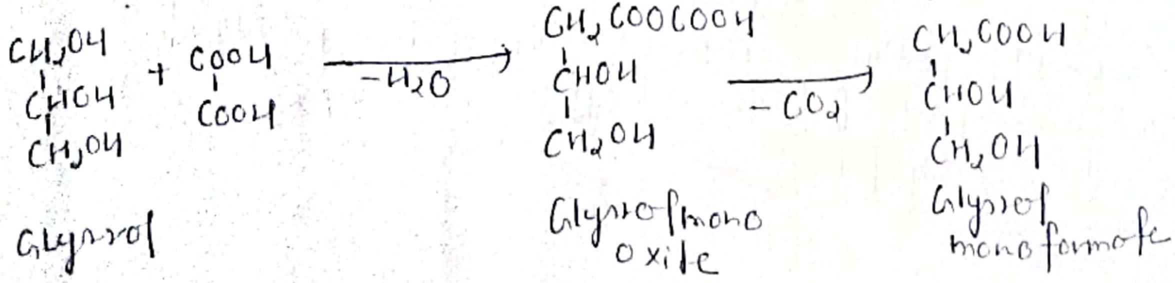
(i) Carboxylic Acid

(o/260c)



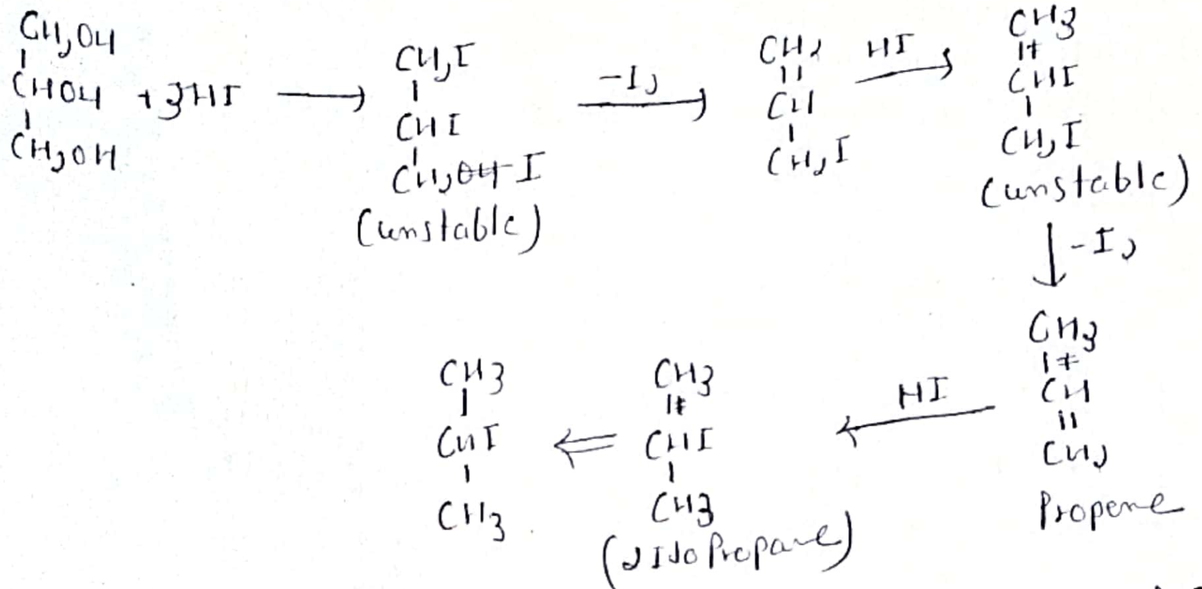
$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\end{array}+\begin{array}{c}COOH\\ |\\ COOH\end{array}\xrightarrow[-2H_2O]{\Delta}\begin{array}{c}CH_2OOC\\ |\\ CHOOC\\ |\\ CH_2OH\end{array}\xrightarrow[-2CO_2]{\Delta}\begin{array}{c}CH_2\\ \|\\ CH\\ |\\ CH_2OH\\ \text{Aryl Alchohol}\end{array}$$

(o/110c)



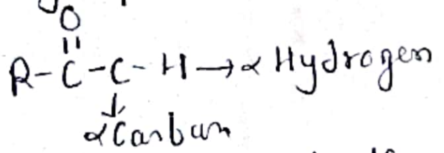
$$\begin{array}{c}CH_2OH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glysrol}\end{array}+\begin{array}{c}COOH\\ |\\ COOH\end{array}\xrightarrow[-H_2O]{}\begin{array}{c}CH_2COOCOOH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glysrol mono oxite}\end{array}\xrightarrow[-CO_2]{}\begin{array}{c}CH_2COOH\\ |\\ CHOH\\ |\\ CH_2OH\\ \text{Glysrol mono formate}\end{array}$$

(11) Glysrol Reacts with HI -



Que-2. Cause of Acidity of α Hydrogen atom -

" The acidity of α Hydrogen is due to the high withdrawing effect of Carboxylic group and resonance Steblization of the Conjugate base."

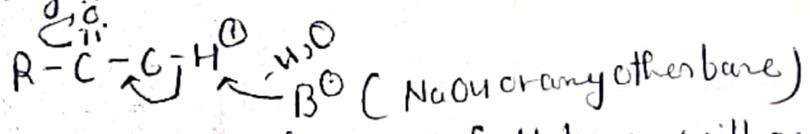


$R-\overset{O}{\overset{\|}{C}}-C-H \rightarrow \alpha$ Hydrogen

α Carbon

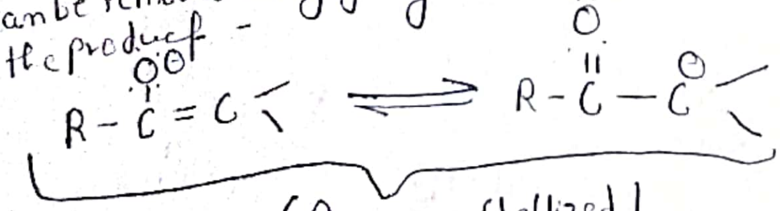
α Hydrogen is Present in the given Compound.

When given Compound reacts with a base -



$R-\overset{O}{\overset{\|}{C}}-C-H^{\oplus}$ $B^{\ominus}$ (NaOH or any other base) H_2O

C-C B⁻¹ will attract C-H e⁻. So Hydrogen will gain positive Charge. So it can be removed easily by any base. and the product -



$R-\overset{O^{\ominus}}{C}=C< \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}<$

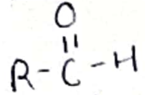
(Resonance Steblized)

So Acidity of α Hydrogen is due to High ~~electronegativity of O~~ withdrawing effect of the Carboxyl group and Resonance Steblization of the Conjugate base"

" So α Hydrogen is of Acidic Nature.",

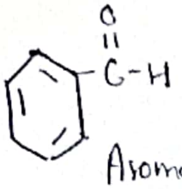
Aliphatic Aldyhydes are more reactive than the Aromatic Aldyhydes of the Same molecular weight.

Sol. Aliphatic Aldihydes and Aromatic Aldyhydes are two board classes of the Aldyhydes. The difference between aromatic aldyhydes and aliphatic Aldyhydes is the interaction between the Carban and Hydrogen atom. In aliphatic Aldyhydes the Band between Carban and Hydrogen atoms are too weak. So they can break easily. So, therefore Aliphatic Aldyhydes are more reactive. In Aromatic Aldyhydes the band between Hydrogen and Carban atom are strong and Carban atoms are arranged in the form of a flat ring. Therefore Aromatic Aldyhydes are more reactive.



$R-\overset{\overset{O}{\parallel}}{C}-H$

Aliphatic Allylyde



Aromatic Aldyhydes

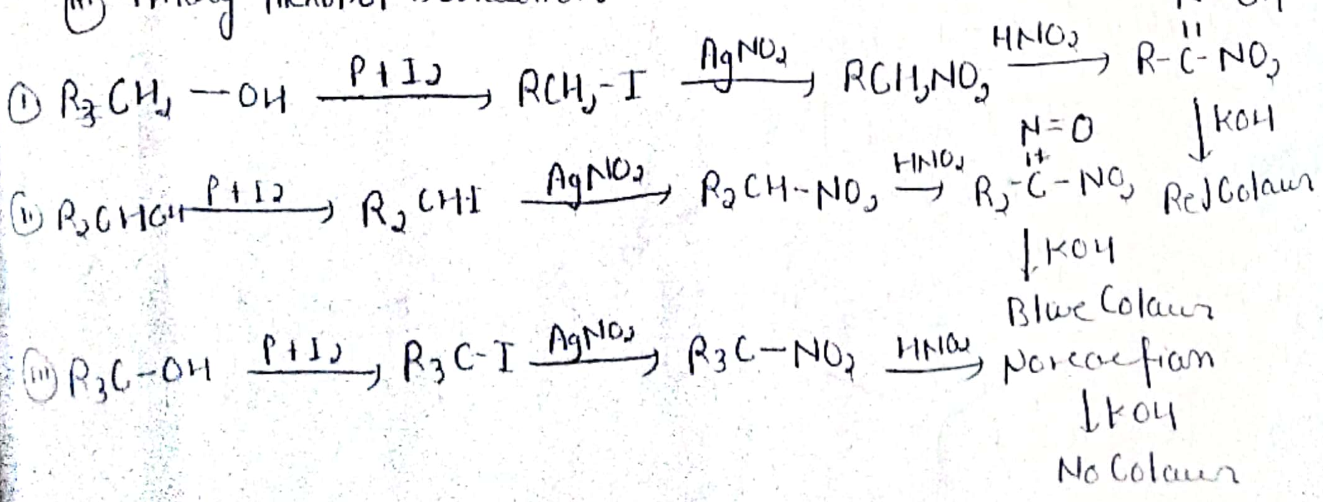
So the Aliphatic Aldyhydes are more reactive towards Nucleophilic addition Reactions because the band between Carban and Hydrogen atoms are weak and can be broken easily where the otherside the Aromatic Aldyhydes are less reactive towards nucleophilic addition reaction because the bands are strong and C-atoms are arranged in the form of a flat ring and hard to break.

There we can say that Aliphatic Aldyhydes are more reactive towards the nucleophilic addition Reaction then Aromatic Aldyhydes of Same molecular weight.

Que- How did you distinguish primary, Secondary and Tritary Alchohols.

Soln. By Victor Mayer Method -

① Primary Alchohol gives Red Colour
(ii) Secondary Alchohol gives Blue Colour
(iii) Tritary Alchohol is Colourless



① $R_3CH_2-OH \xrightarrow{P+I_2} RCH_2-I \xrightarrow{AgNO_2} RCH_2NO_2 \xrightarrow{HNO_2} R-\overset{\overset{N-OH}{\parallel}}{C}-NO_2 \xrightarrow[\downarrow]{KOH}$ Red Colour

(ii) $R_2CHOH \xrightarrow{P+I_2} R_2CHI \xrightarrow{AgNO_2} R_2CH-NO_2 \xrightarrow{HNO_2} R_2-\overset{\overset{N=O}{|}}{C}-NO_2 \xrightarrow{KOH}$ Blue Colour

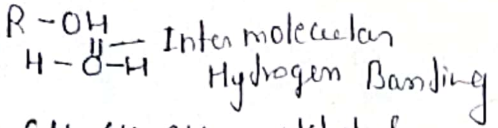
(iii) $R_3C-OH \xrightarrow{P+I_2} R_3C-I \xrightarrow{AgNO_2} R_3C-NO_2 \xrightarrow{HNO_2}$ No reaction $\xrightarrow{KOH}$ No Colour

Qu. Boiling Paint of Alchohols is Higher then the Alkanes of the Same molecular weight.

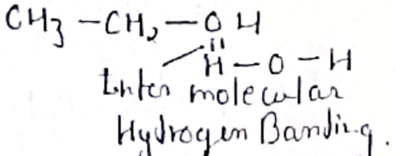
Soln ① In Alkanes the Intermolecular Bands are anly Van der Waals forces (weak) where in Alchohol the Intermolecular Bands are Hydrogen Band due to the high electronegativity of Oxygen atom. So more energy is required to break Intermolecular Hydrogen Band then Van der Waal's forces.

(ii) Alchohols can easily make Hydrogen Band with the molecules of the water due to polarization. Where the other Side the Alkanes are unable to make Hydrogen Band with water molecule because of No polarization.

Let we have R-OH as Alchohol.
When we put it in water.



Let we have CH_3-CH_2-OH as a alchohol.
When it reacts with H_2O.



where the corrospanding Alkane $CH_3 - CH_3$ is unable to form any Hydrogen Band with water.

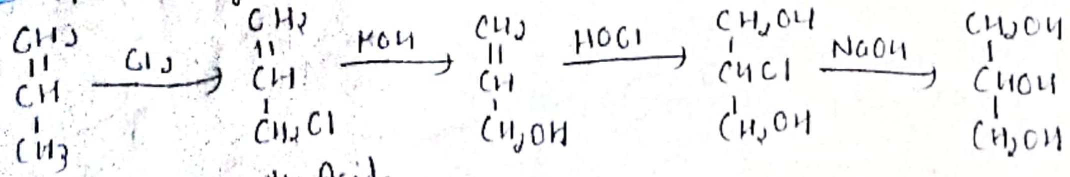
(iii) When the molar mass of Alchohol Increases, So the Vanderwalls forces increses. So the Boiling Paint also increses.

Conclusion -

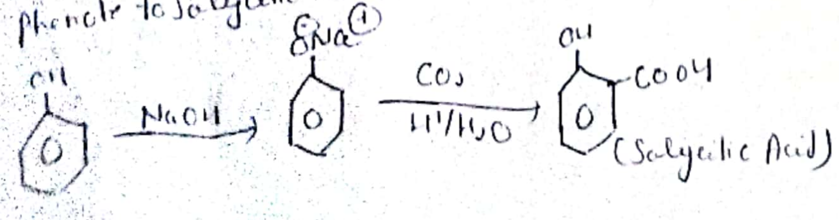
Alchohols
① Intermolecular Hydrogen Banding.
(ii) High Polarization
(iii) Strong Wanderwalls forces.

Alkanes
① No Intermolecular Hydrogen Banding.
(ii) No Polarization.
(iii) Weak VanderWaal's forces.

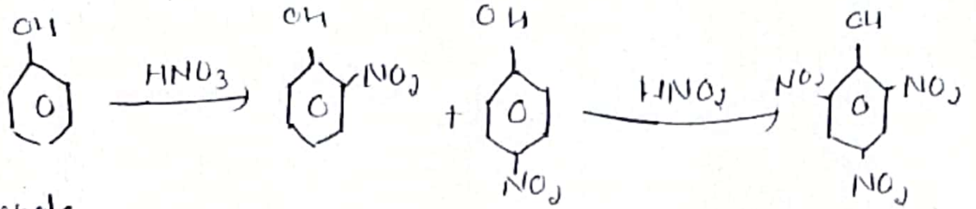
Q. (i) Propene to Glyerol -



(ii) Phenole to Salycilic Acid.



(iii) Phenole to Pipric Acid -

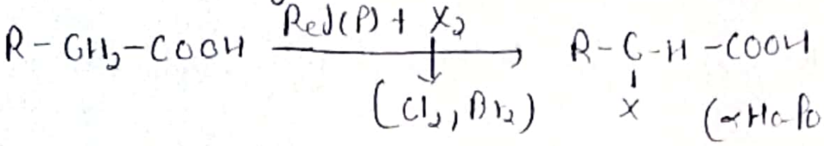


Phenole

Pipric Acid
(2,4,6 Nitrophenole)

Q- Hale Vol Hard Zelansky (Halogination of COOH) -

" Hale vol Hard Zelansky is a Chemical reaction in Organic Chemistry to convert Carboxylic Acid to α Halo Carboxylic Acid. "



$$R-CH_2-COOH \xrightarrow[(Cl_2,\ Br_2)]{Red(P)\ +\ X_2} R-\underset{X}{\underset{|}{C}}-H-COOH$$

(α Halo Carboxylic Acid)

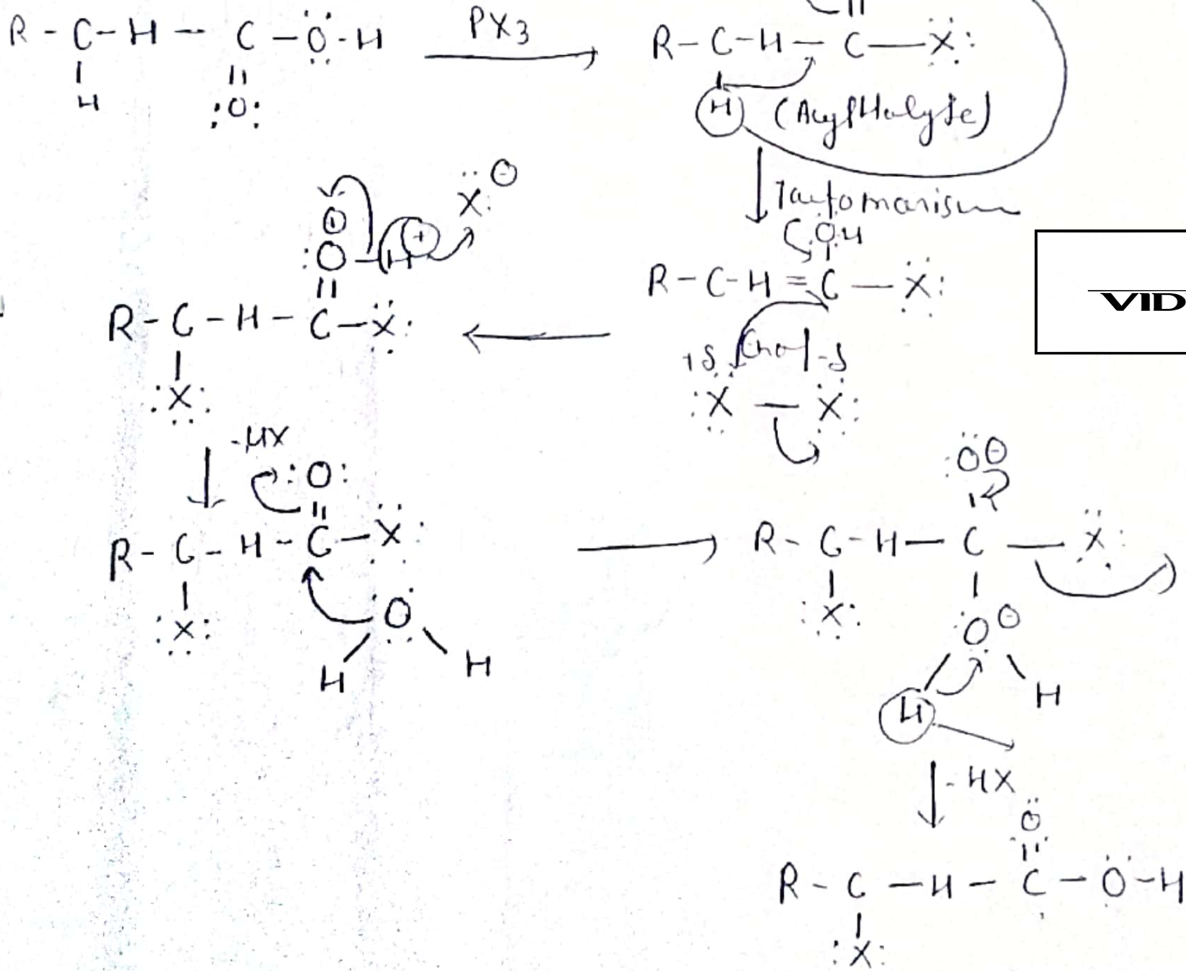
Machenism - (i) Formation of PX_3

(ii) Carboxylic Acid reacts with PX_3 and formation of Acyl Halyde

(iii) Taufomarism to the Enol form and reaction with Halogens.

(iv) Hydrolysis yeils to the formation of the α Halo Carboxylic Acid.

$$P + X_2 \longrightarrow PX_3$$



α Halo Carboxylic Acid

Q. Nucleophilic Substitution Reactions -

"A reaction in which a Strong Nucleopite replaces a weak Neucleophile."

① There are two types of Nucleophilic Substitution Rxns.

(i) SN_1 reaction

(ii) SN_2 reaction.

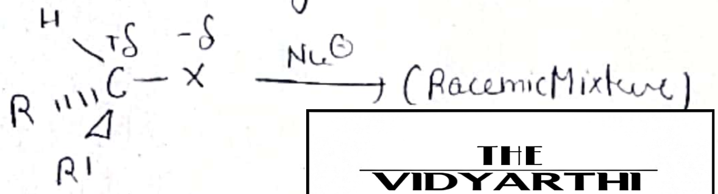
① SN_1 reaction -

Substitution — S N ① – unimolecular
Nucleophilic

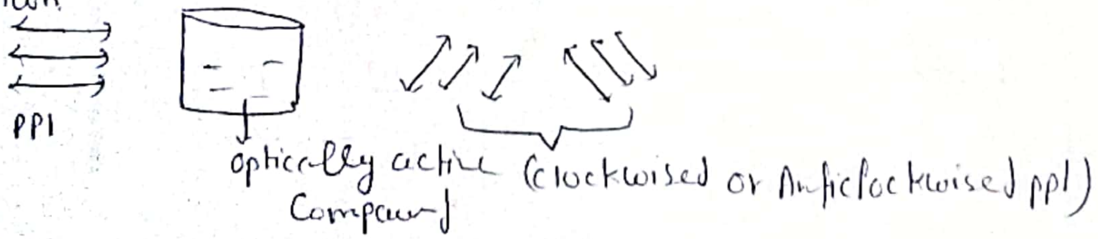
So we can say SN_1 reaction as unimolecular Nucleophilic Substitution Rxn.

[Molecularity or Rate of Reaction - 1]

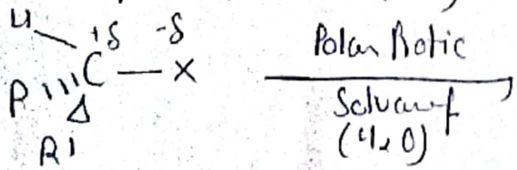
Mechanism - Firstly we take a optically active Compound (like Chiral Carbon.)

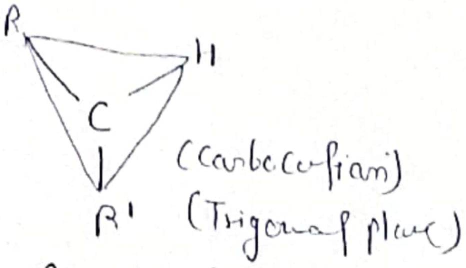


Optically Active Compound - "Optically active Compounds are the Compounds who turns ppl in to Clockwise or anticlockwise direction"



(i) Step ① (Formation of Carbocation) -

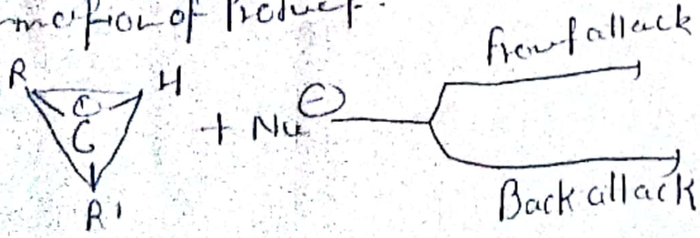


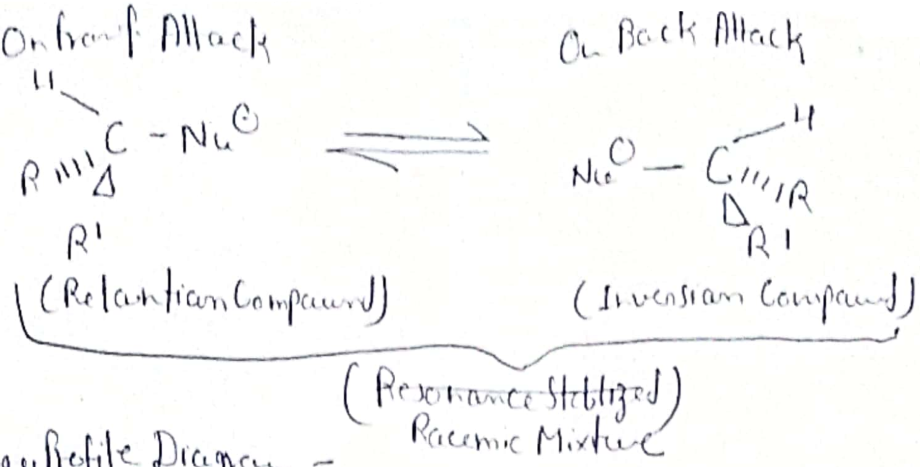


This Step is known as Rate Determining Step.

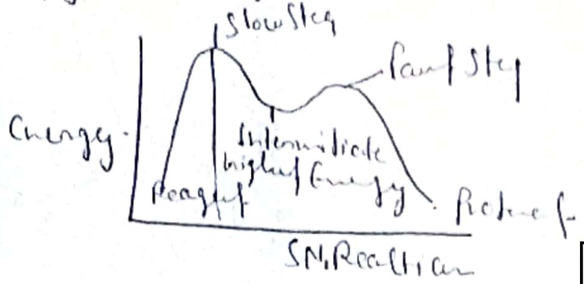
Rate of Reaction = $k[C-X]^1 = 1$ (Slow Step)

(ii) Formation of Product.





Energy Profile Diagram -

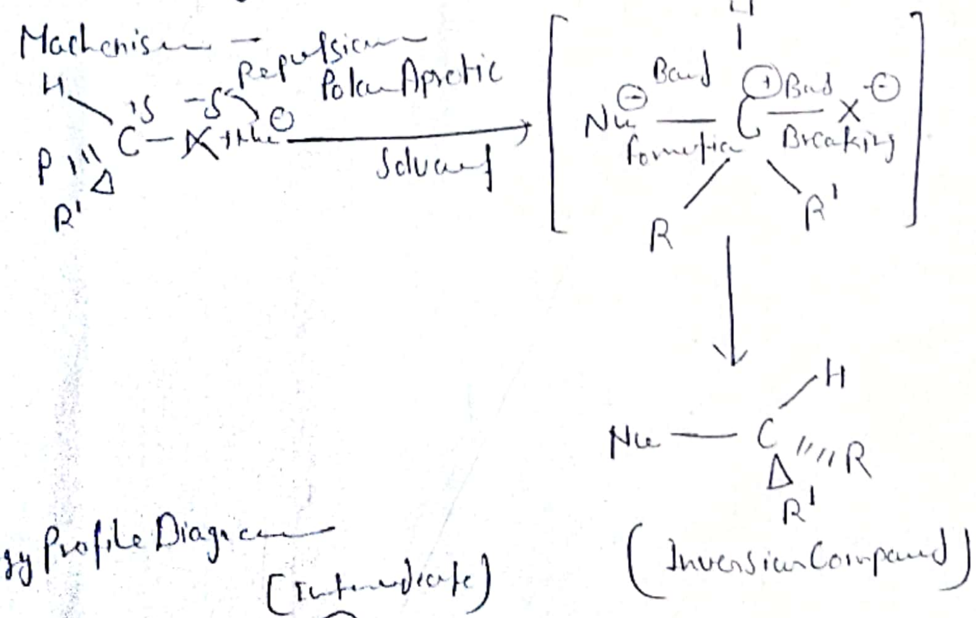


SN2 reaction -

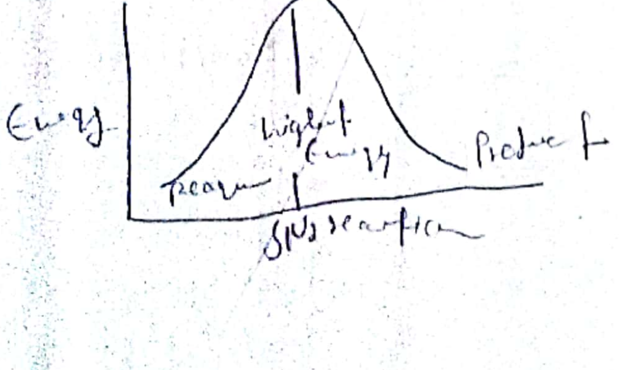
Substitution - SN2 - Bimolecular
Nucleophilic

So we can say SN2 as Bimolecular Nucleophilic Substitution Reaction.

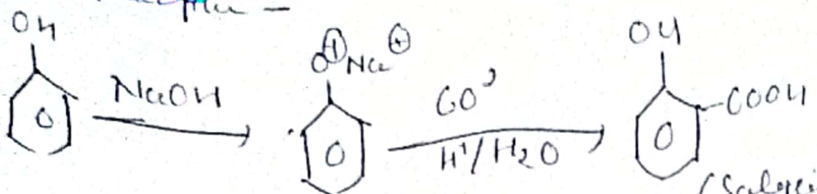
Mechanism -



Energy Profile Diagram



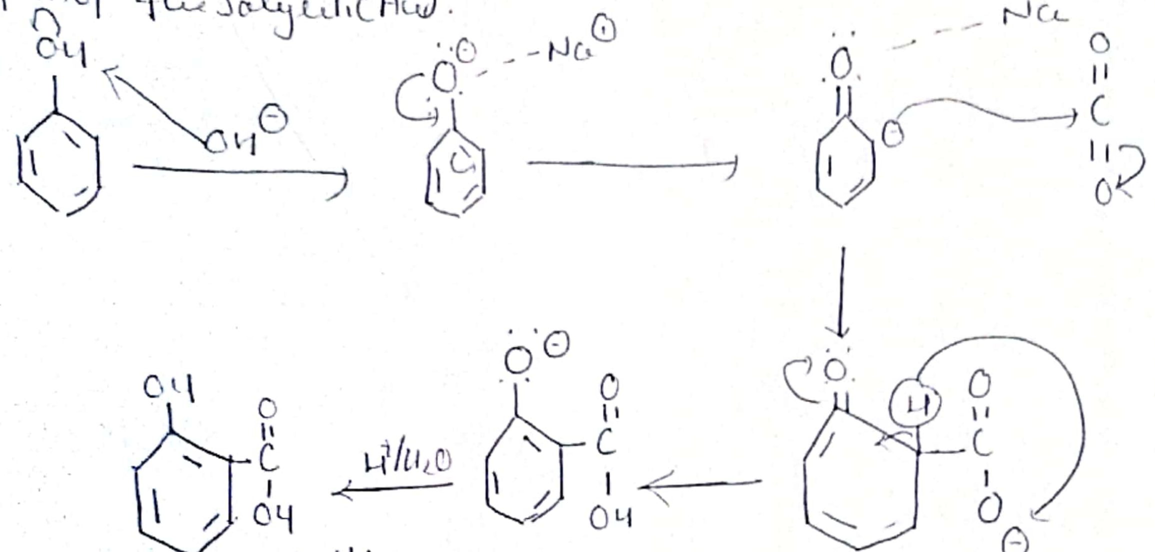
Kolbe Reaction –



(Salycilic Acid)

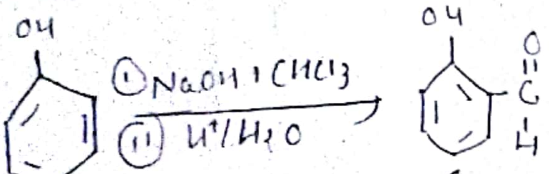
Machenism –

“Machenism of Kolbe reaction Starts with when Sodium phinoxite is allowed to absorb CO2 at 100 atm and 125°c temp. Now we get a unstable intermidiate. This intermidiate goes through a proton Shift leading to the formation of Sodium Salycilate. Now Acidification yeils to the formation of the Salycilic Acid.”

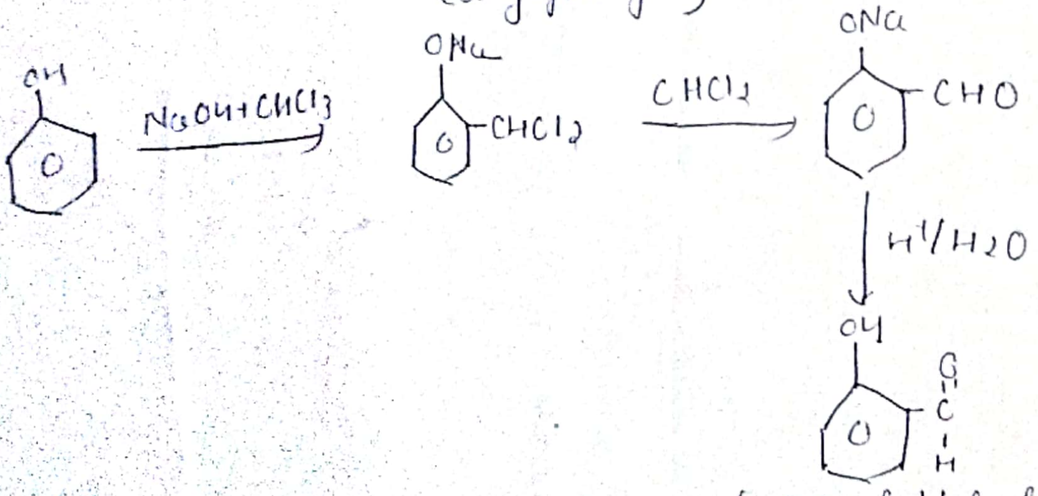


(Salycilic Acid)

Ra-Rimer Timen –



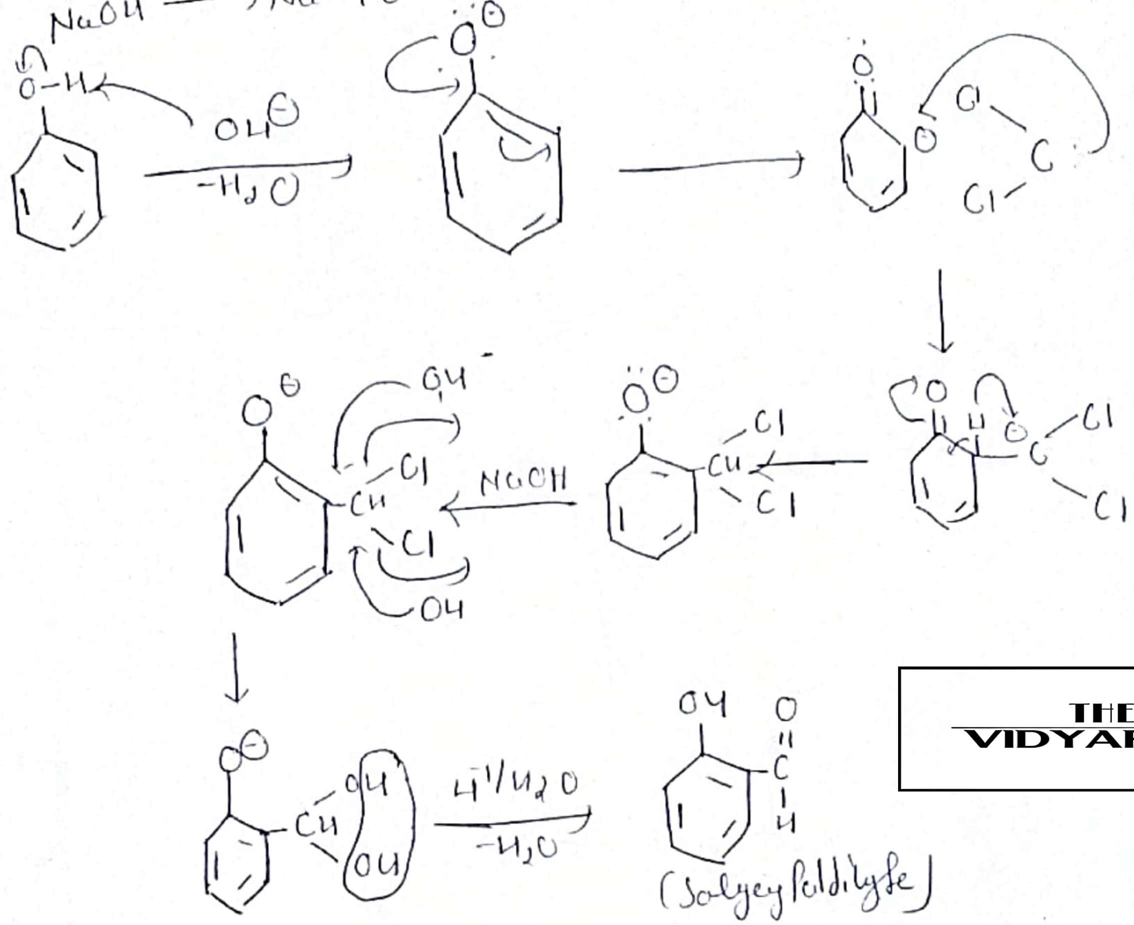
(Salycyaldihyde)



(Salicylaldyhyde)

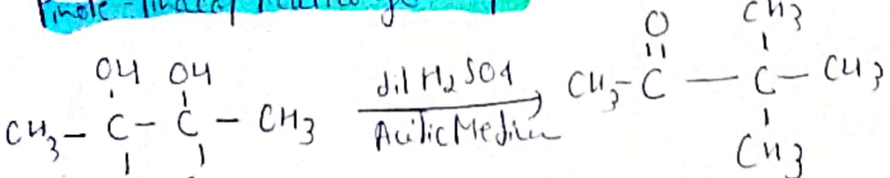
Machenism —

$NaOH \longrightarrow Na^{\oplus}, OH^{\ominus}$



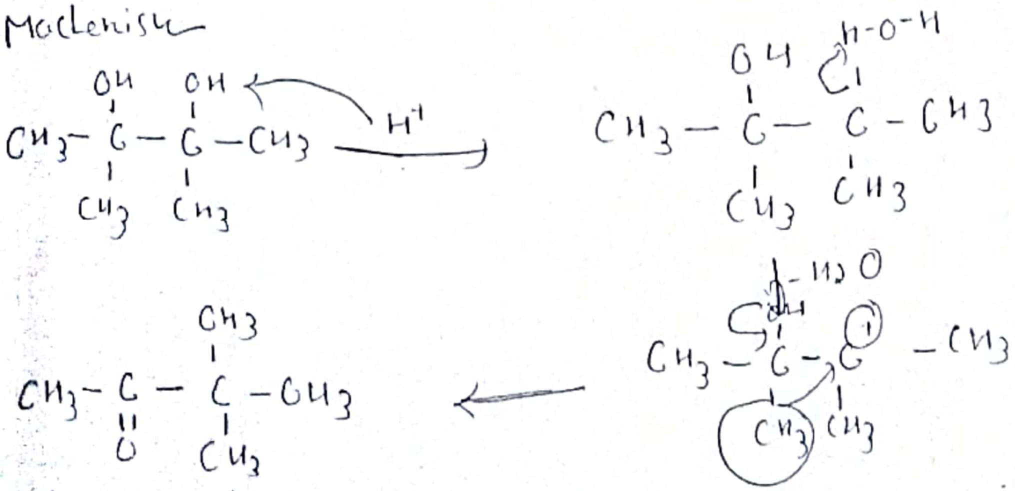
(Salicylaldehyde)

Pinole - Pinacol Rearrangement :-



Pinacole

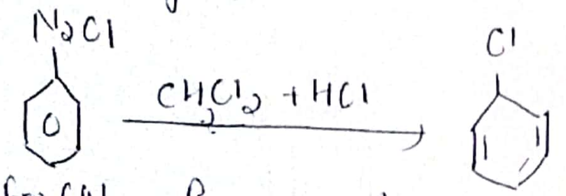
Machenism



(Pinacol)

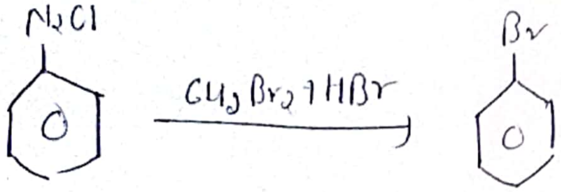
1.2 diol to Carbonyl Compound)

ChloroBanzeene, BromoBanzeene from Diazonium Salt -
(SandMayer)

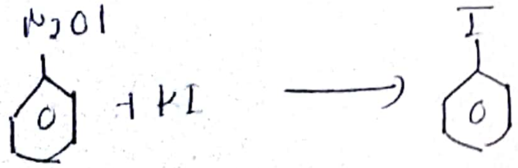


(For Chloro Banzeene)

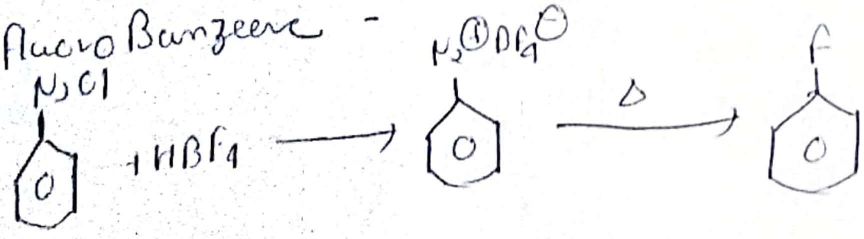
BromoBanzeene -



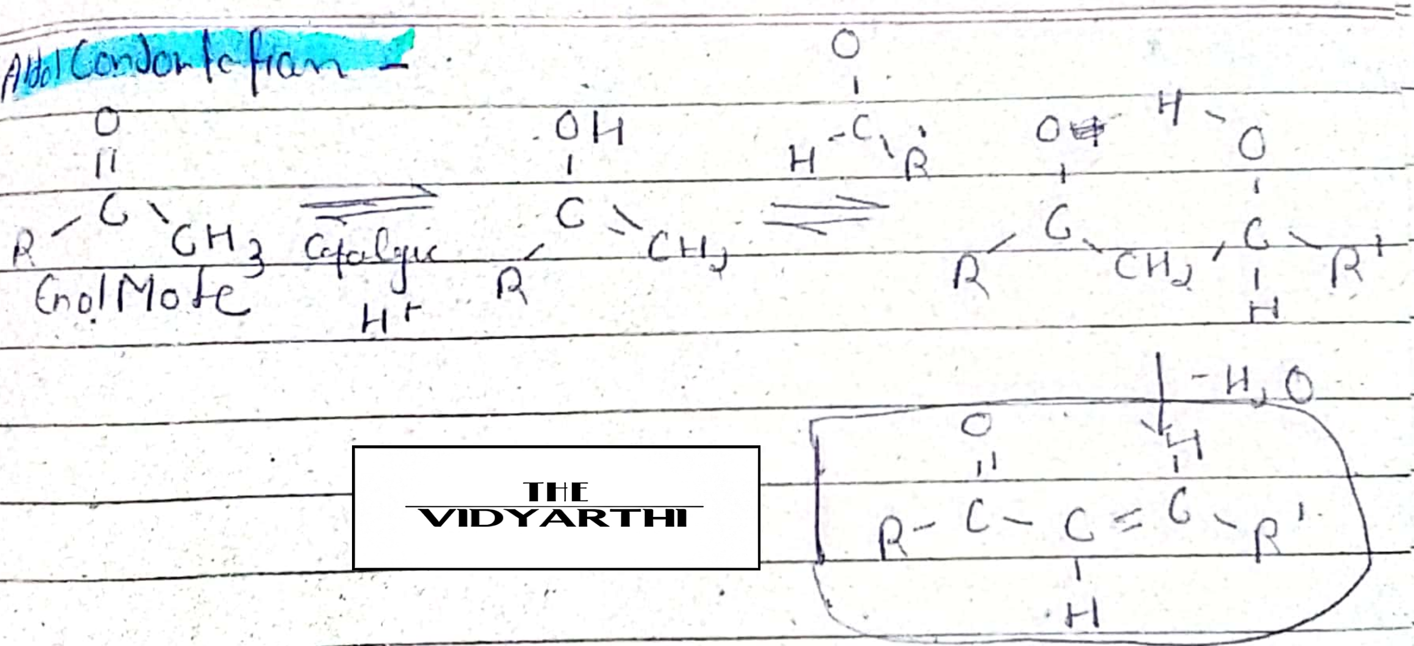
IdoBanzeene -



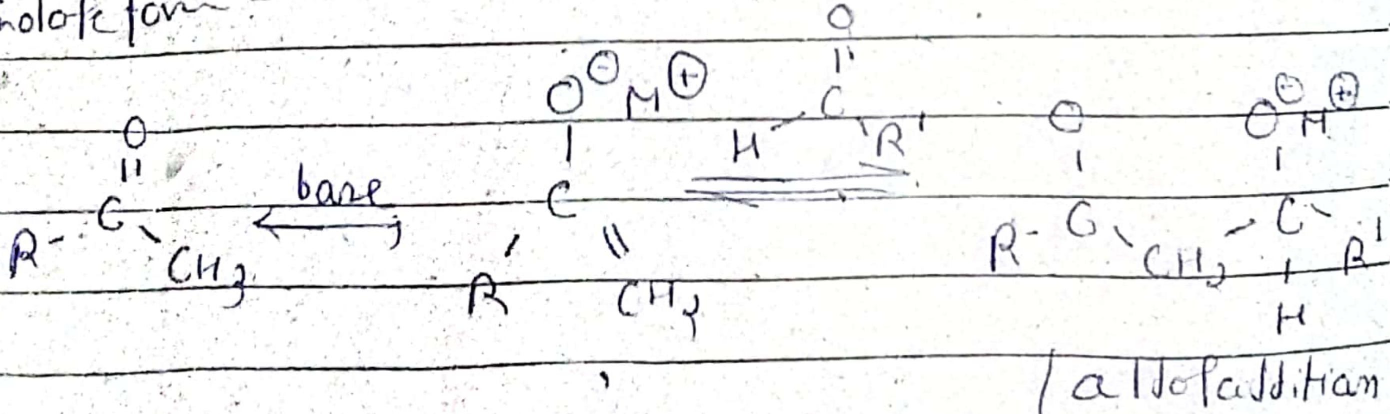
FluoroBanzeene -



Aldol Condensation -



Enolate form -

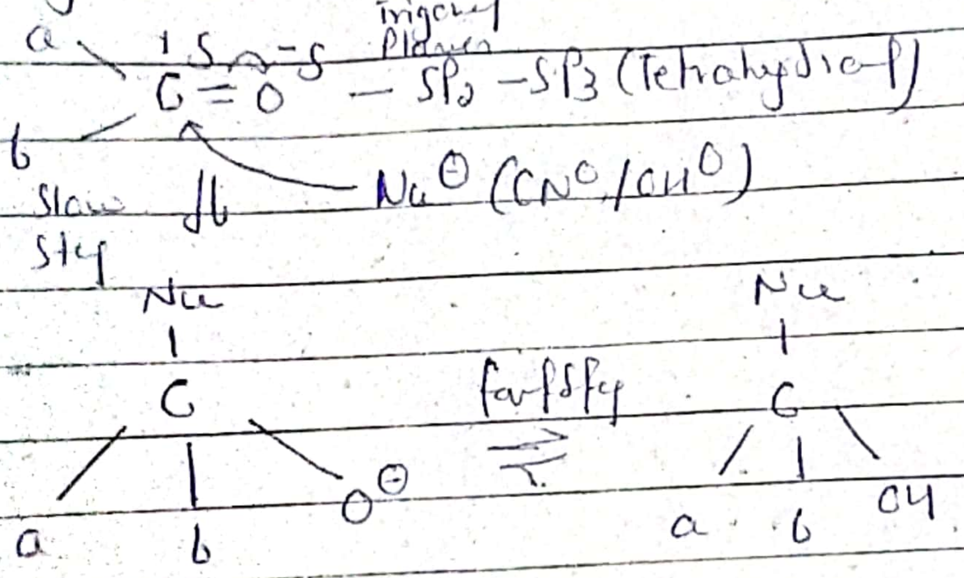


(aldol addition Product)

Aldehyd and Ketone - ① Nucleophilic Addition reaction
Nu⊖
(Carbonyl group) | Benzene - Electrophilic Substitution

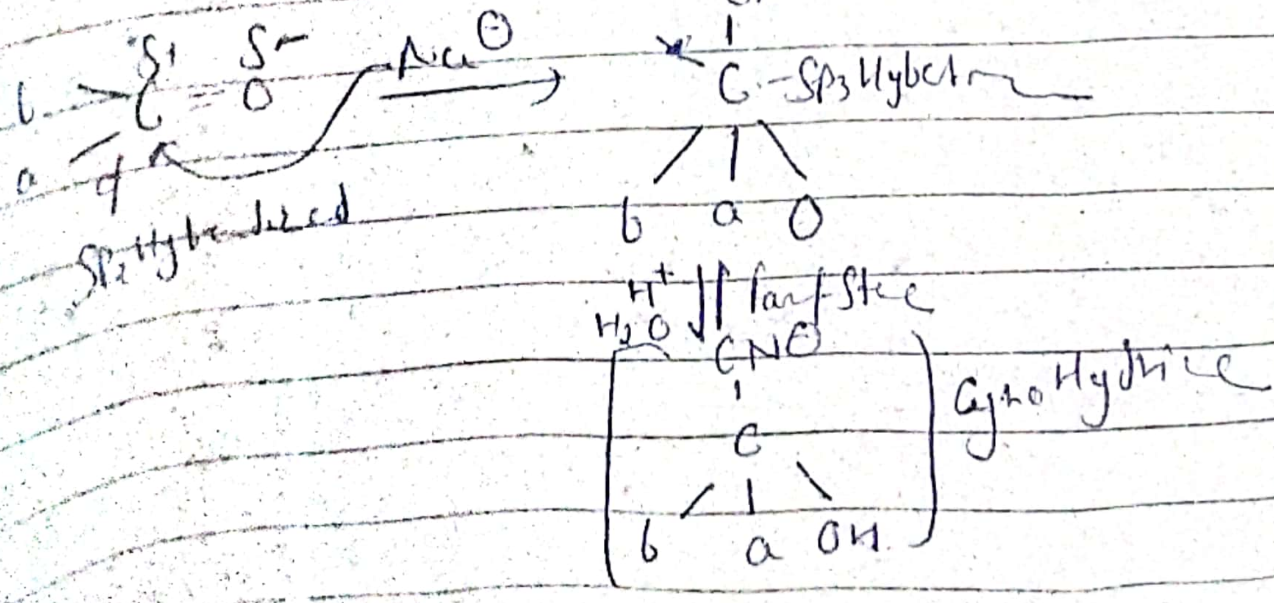
Que- Explain the acid and base catalysed Nucleophilic addition of Carboxyl Compounds.

Soln.

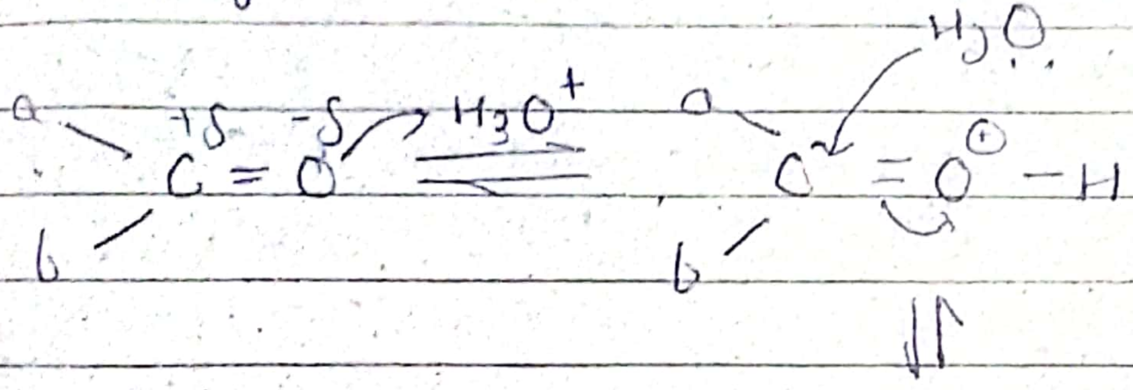


Addition of HCN: (Base Catalysed) -

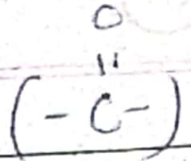
$HCN + \underset{\text{(Base)}}{OH} \longrightarrow \underbrace{CN^{\ominus}}_{\text{Nucleophile}} + H_2O$



Acid Catalysed –

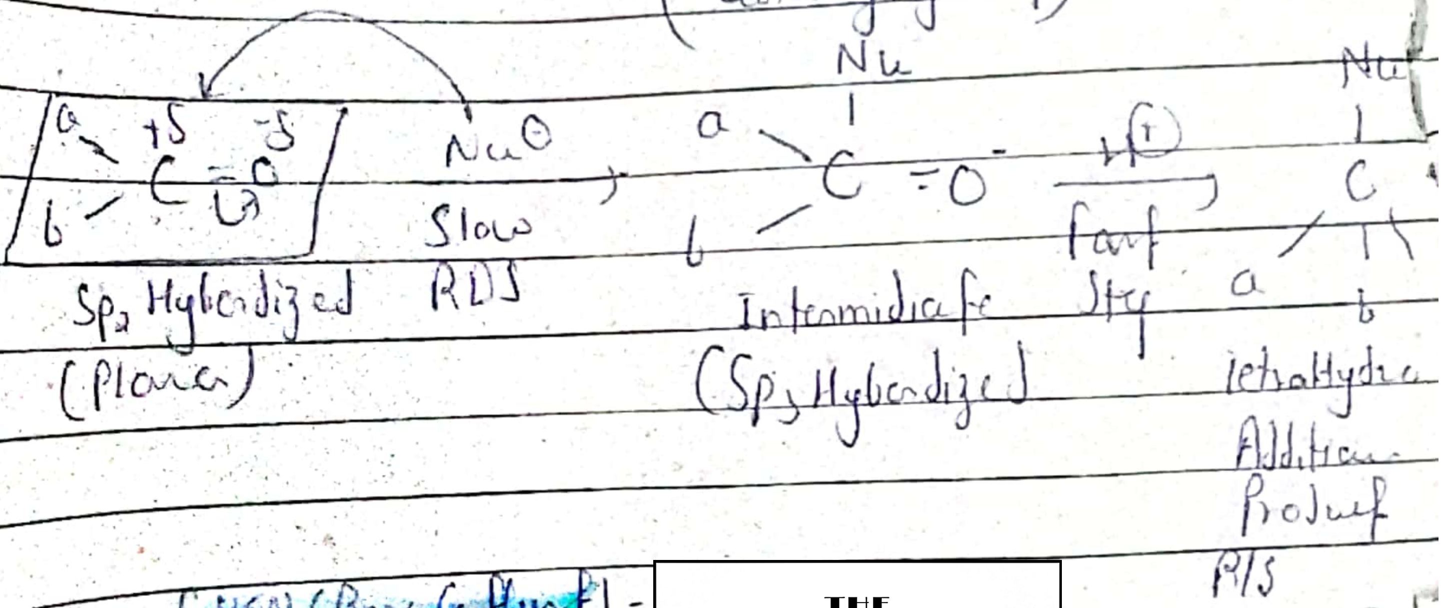


① Nucleophilic addition Reaction –



$\left(-\overset{O}{\overset{\|}{C}}-\right)$

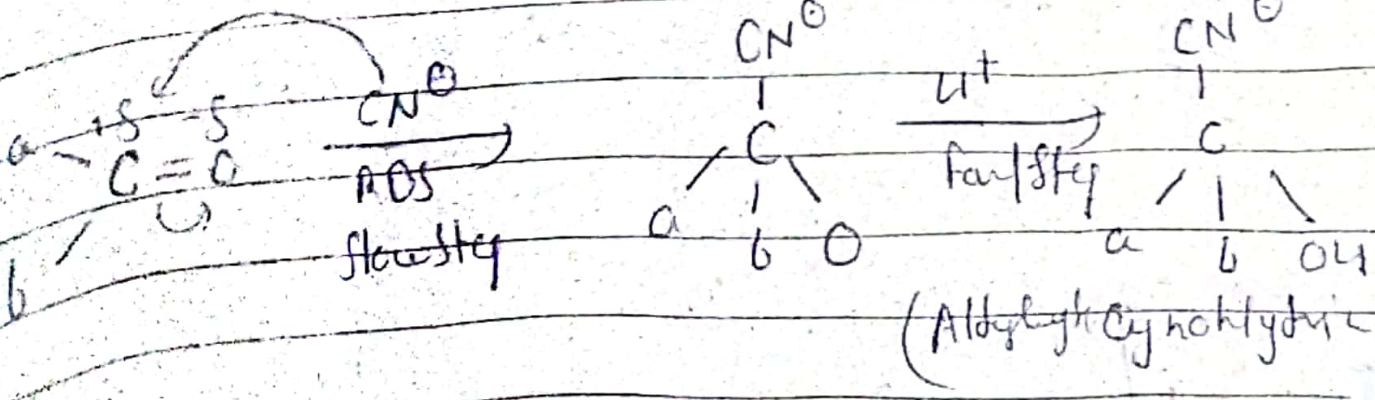
(Carbonyl group)



① Addition of HCN (Base Catalyst) –

[Cyanohydrin] –

$HCN + \underset{(Base)}{OH^-} \rightarrow \underbrace{CN^{\ominus}}_{Nucleophile} + H_2O$



Phenole - Compound in which OH group is directly attached to an aromatic Carbon, like Benzene ring.

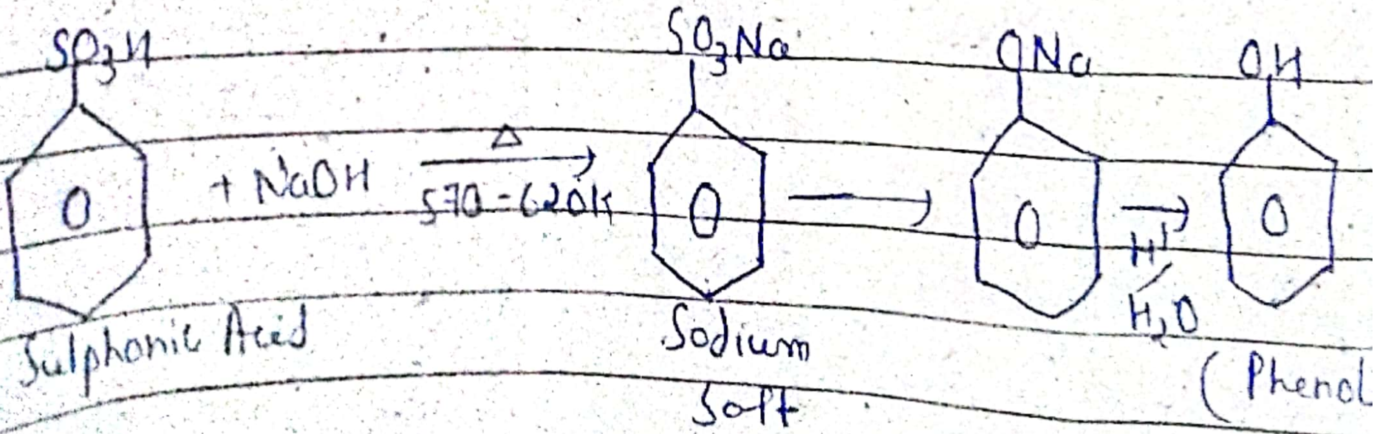
(Phenole)

O atom banded to a Sp_2 Hybendized ~~C atom~~ aromatic C atom and H atom via σ band.

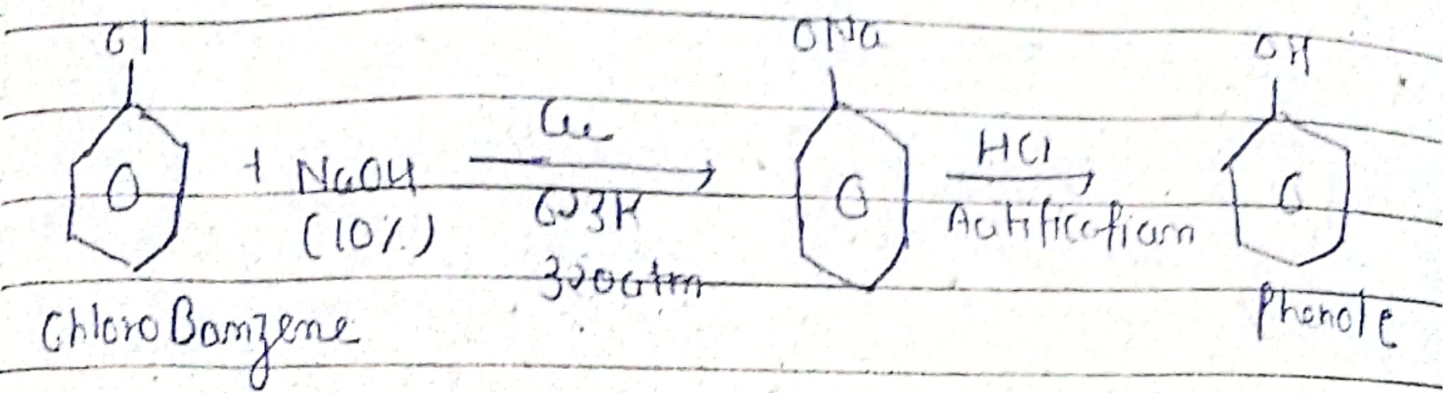
Both C-O and O-H are polar due to High electronegativity of O-atom.

Methods of Preperation of Phenole -

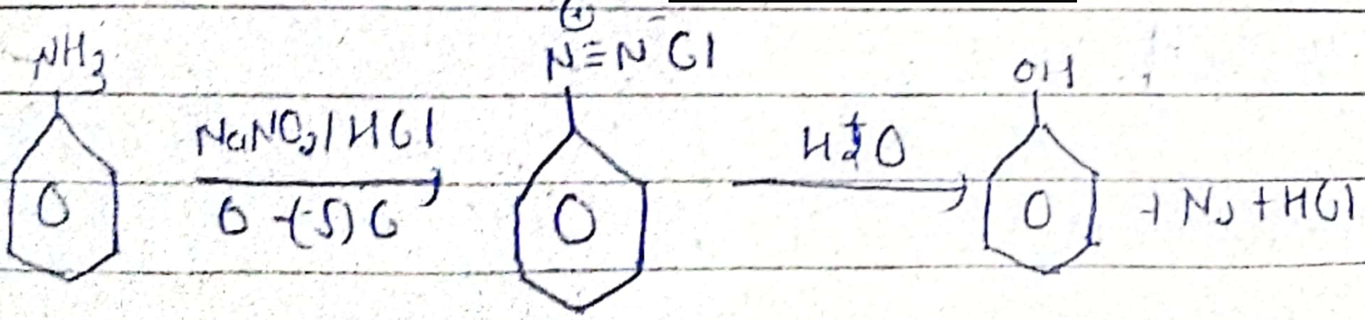
① from Aryl Sulphonic Acids -



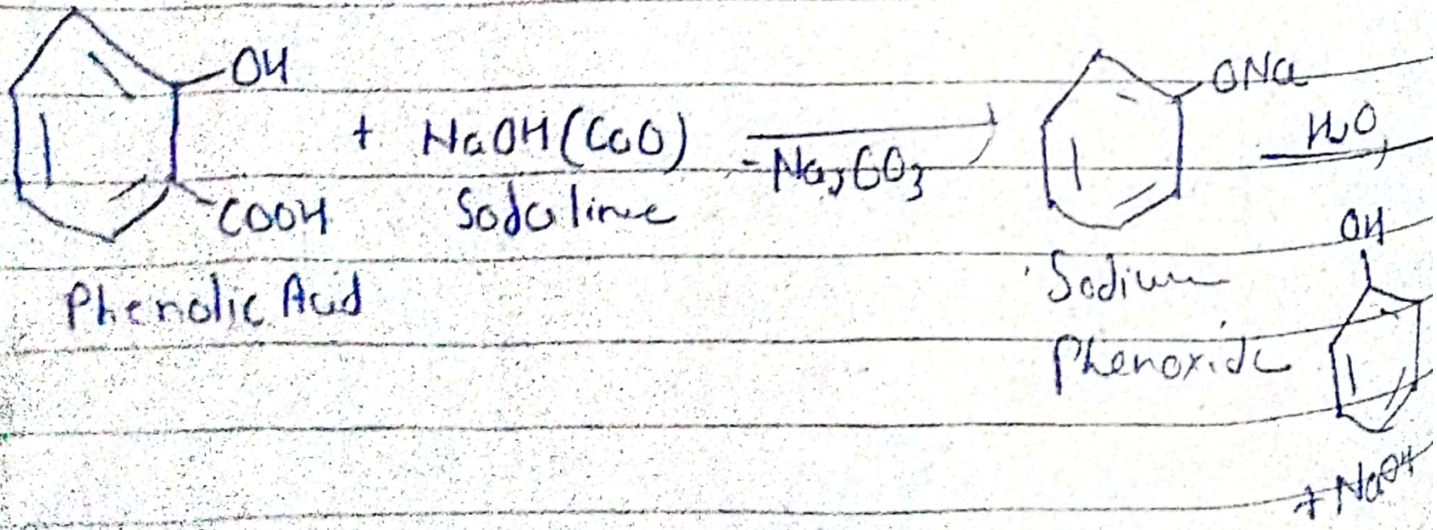
) From Halo Arenes -



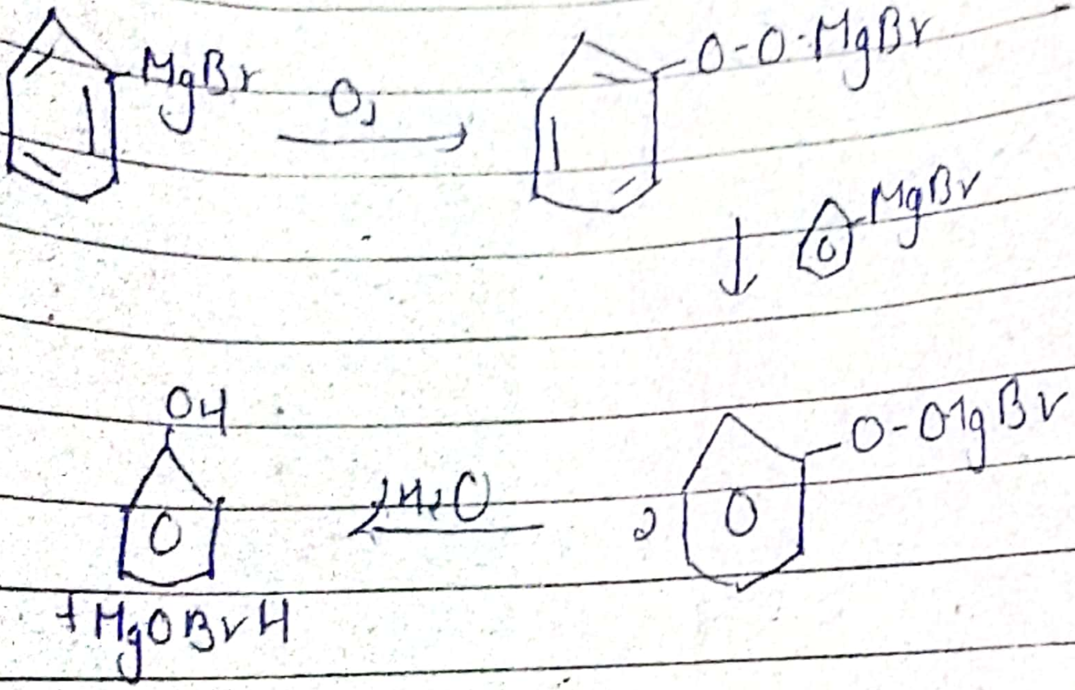
) Hydrolysis of Dyzonium Salt -



Decarboxylation of Phenolic Acid -



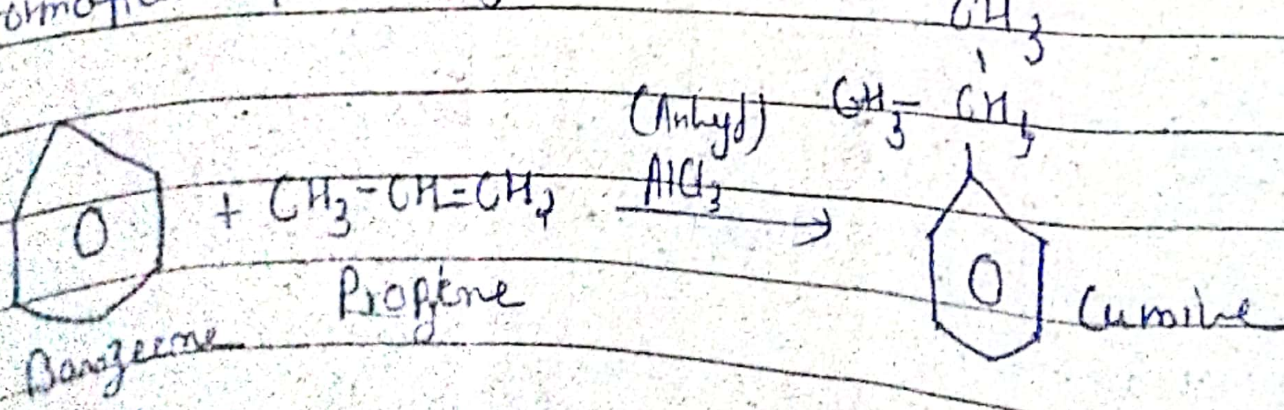
5. Oxidation of Grignard Reagent followed by hydrolysis



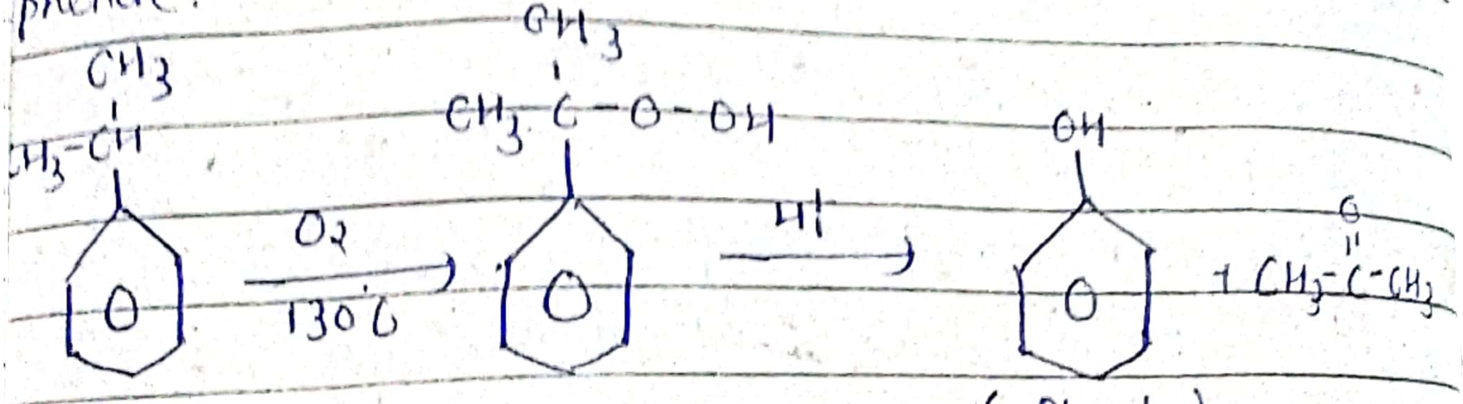
Commercial Preperation of Phenole -

③ from Cumene -

formation Of Cumene by Fridel Craft rxn -



Cumine is Oxidised at 130°C and pressure of metal Catalyst. gives phenole.



(Cumine)

(Phenole)

Physical Properties of Phenole -

Higher boiling point then arenes, haloarenes and ethers of the same molecular weight. (Due to intermolecular H Bond.")

Pure Phenole is white crystline

Disinfectant Smell.

Cause immidiate white blistering to the Skin.

White and Colourless.

Soluble in organic solvant like alchohol but not soluble in water.

Boiling Point increases with the increasement of C atoms.
(Increase in Van der Waal forces)

Acidic Characters of Phenole -

① Phenole is Strong Acid. (than Alchohol)

(ii) It turnes Blue litmus red.

(iii) React with metals to librating Hydrogen.

(iv) Do not react with Carbonates and biCarbonates.

(v) Behaves as acid due to the presence of more polar O-H group in them.

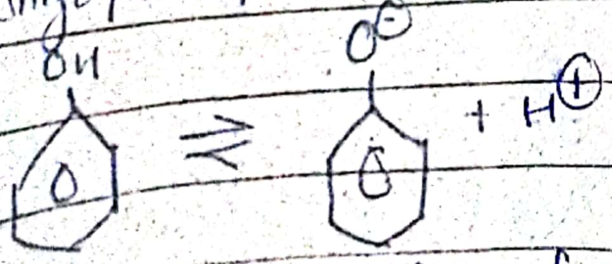
(vi) Phenole as well as Phenoxide ion are resonance stablized.

Acidic Charecteristics of Alchohol and Phenole -

① Ionization of Alchohol -

$$R-OH \rightleftharpoons RO^{\ominus} + H^{\oplus}$$

(ii) Ionization of Phenol -



(i) In Alkoxide - localization of ⊖ change an octane.

(ii) In Phenole dilocalization of ⊖ change an Octane.

Effect of Substances ans Acidity of Phenole -

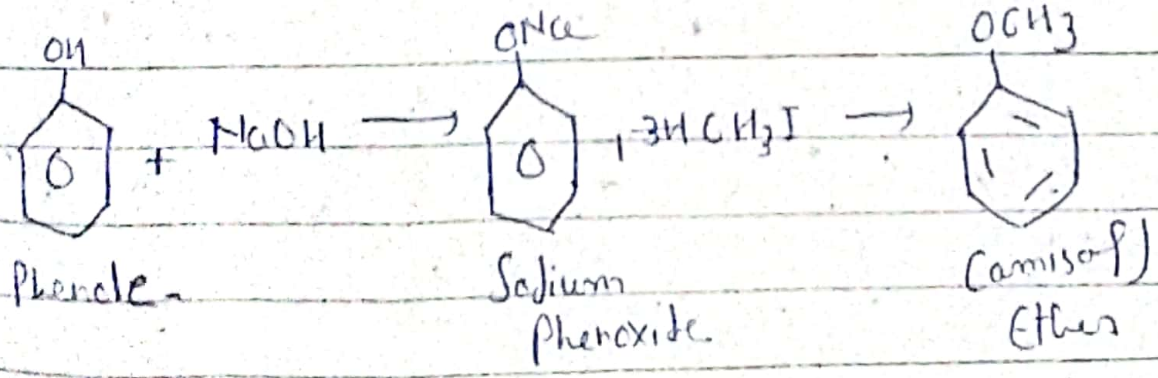
e^- withdrawing group such as nitrogroup enhances the acidity of phenole.

e^- withdrawing group works more frequantly on ortho and para position.

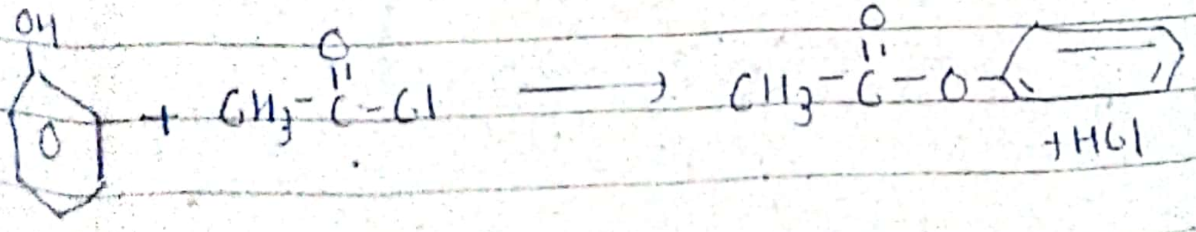
e^- releasing group like alkyl group donot favour the formation of phenoxide ion, decreases the acidity of the phenole.

Reactions of Phenole -

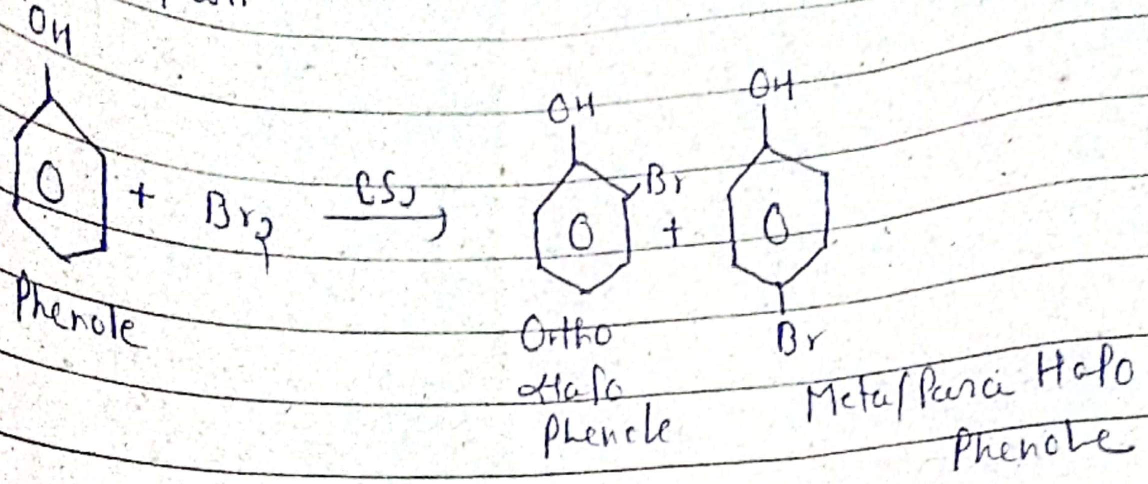
Williamson Synthesis -



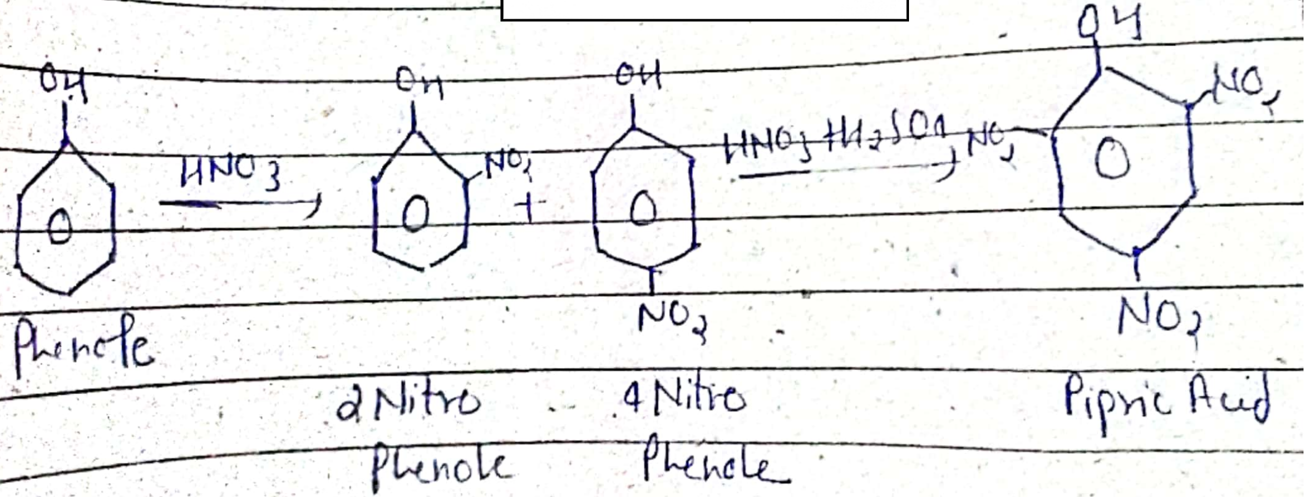
Esterification -



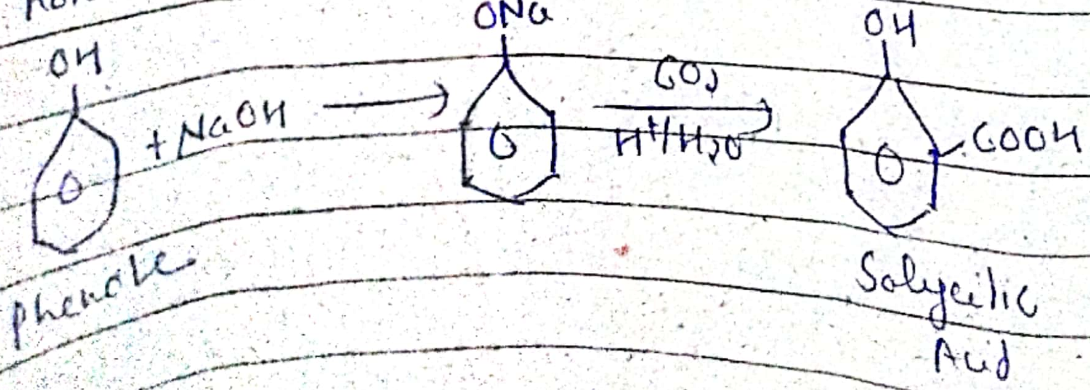
(iii) Halozininafiam -



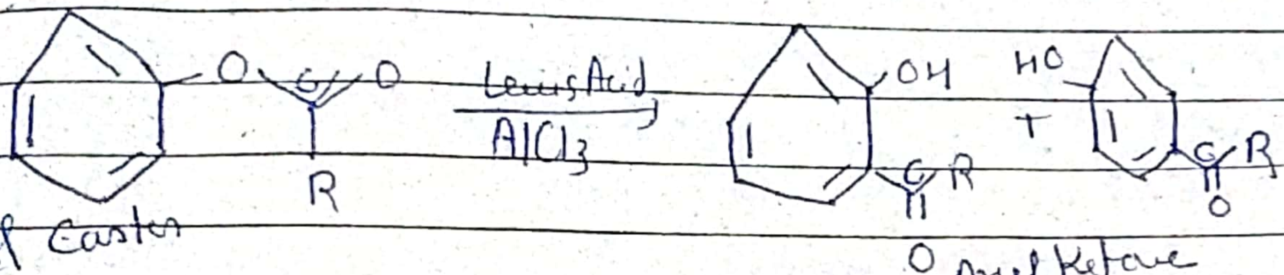
(iv) Nitratiam of Phenole -



(v) Kolbe —



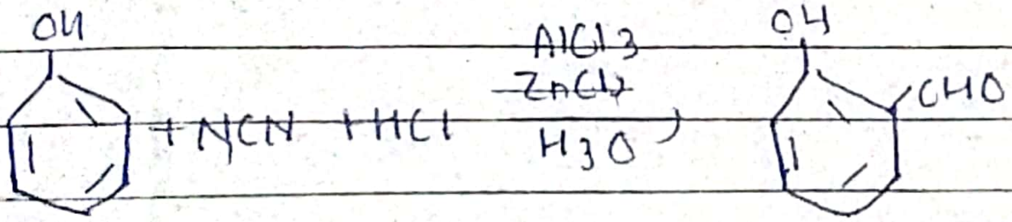
vi) Fries Rearrangement -



Aryl Easter

Hydroxy Aryl Ketone

vii) Gaterman Reaction -



Phinole

Salicylaldehyde

) Rimas Timan -