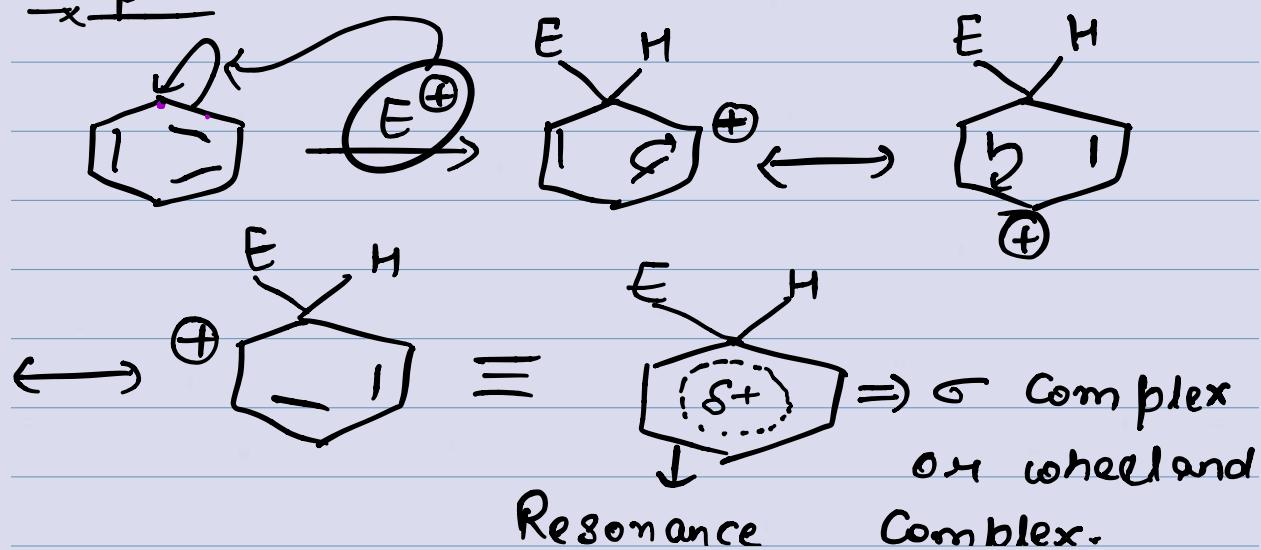


## Aromatic Hydrocarbons.

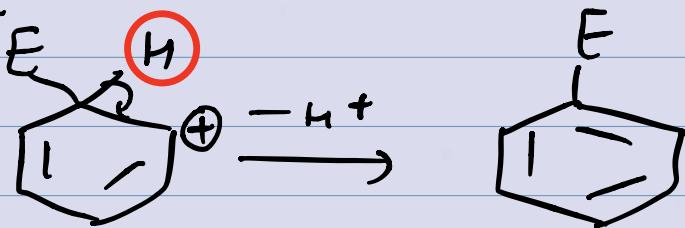
- \* In aromatic hydrocarbons we will study about benzene and its derivatives
- \* Benzene and its derivatives behaves as nucleophiles.
- \* Hence they give electrophilic substitution rxns.
- \* They will not give electrophilic addition rxns because if they try to do so then aromatic character of benzene will be destroyed.

### Step-I



hybrid.

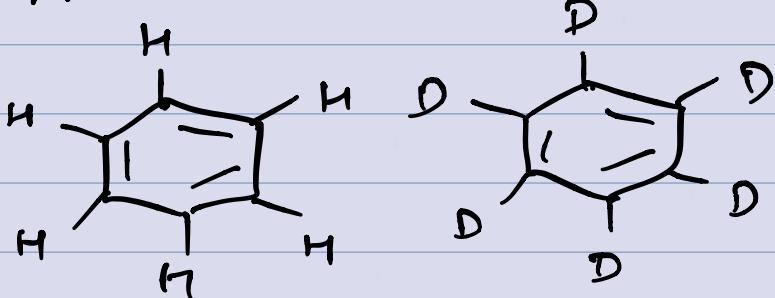
Step-II :-



\* Generally attack of electrophile on benzene is R.D.S. Not always

# \* Kinetic Isotopic effect :-

\* If Step-I is R.D.S. { Attacking of electrophile? then Kinetic Isotopic effect will not be observed.

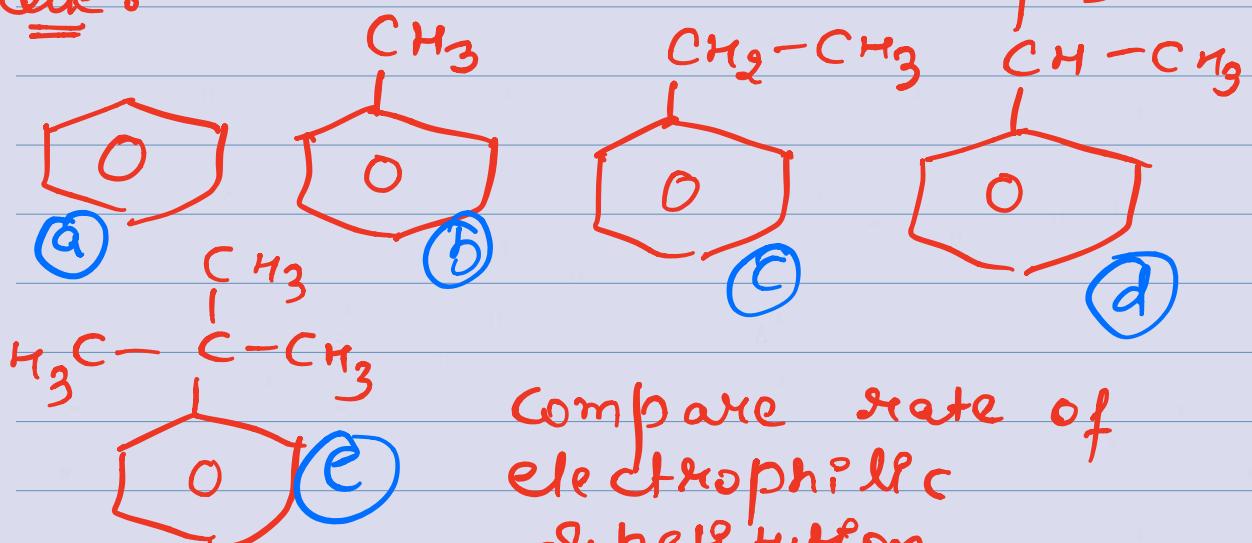


\* If 2<sup>nd</sup> step is R.D.S then Kinetic Isotopic effect will be observed.

\* As Rate of electrophilic Substitution is directly

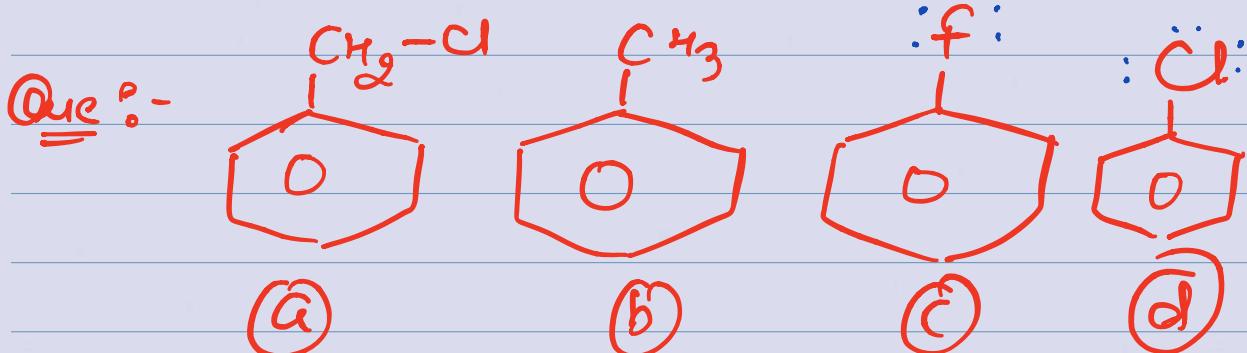
proportional to  $e^-$  density of the ring, hence more will be the electron density on the ring more will be the Rate.

Ques 8-



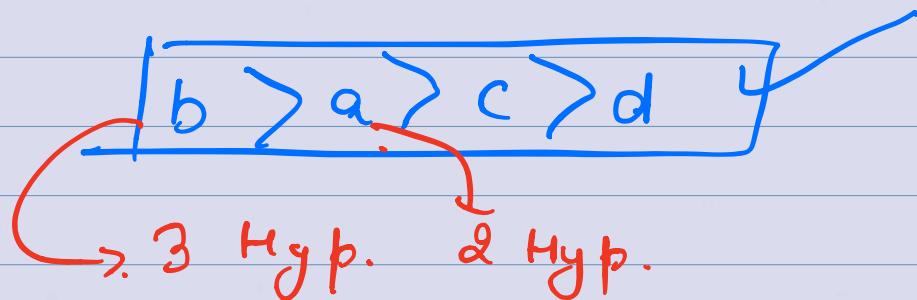
$$[b > c > d > e > a]$$

Ques :-



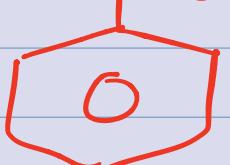
Solm :-

$$\boxed{b > c > d > a}$$



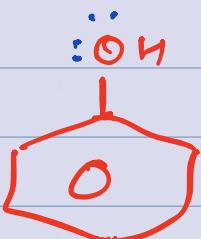
Ques :-

i)  $\text{H}_2\text{O}$



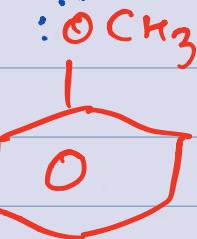
(a)

ii)  $\text{OH}$



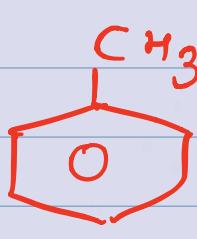
(b)

iii)  $\text{OCH}_3$



(c)

iv)  $\text{CH}_3$

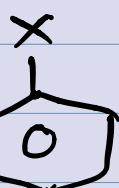
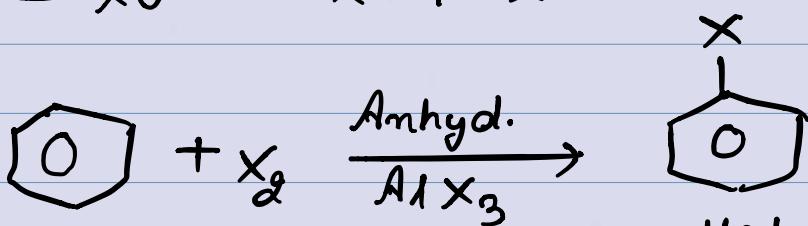


(d)

$$\boxed{a > b > c > d}$$

max<sup>n</sup> + M

# Halogenation of benzene :-

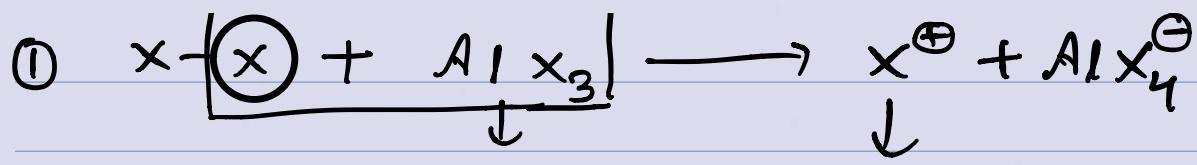


Halo benzene

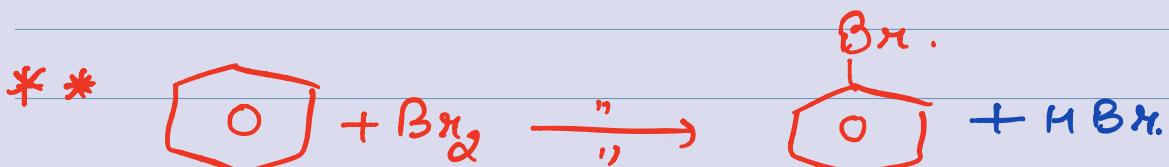
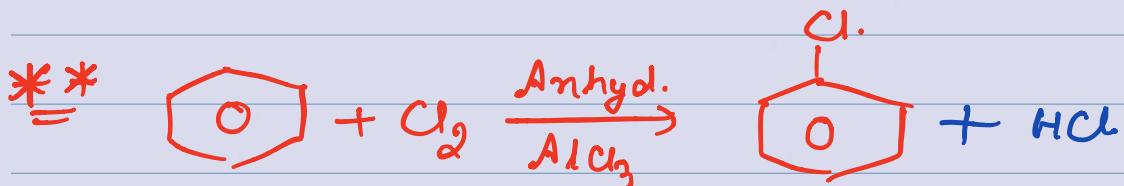
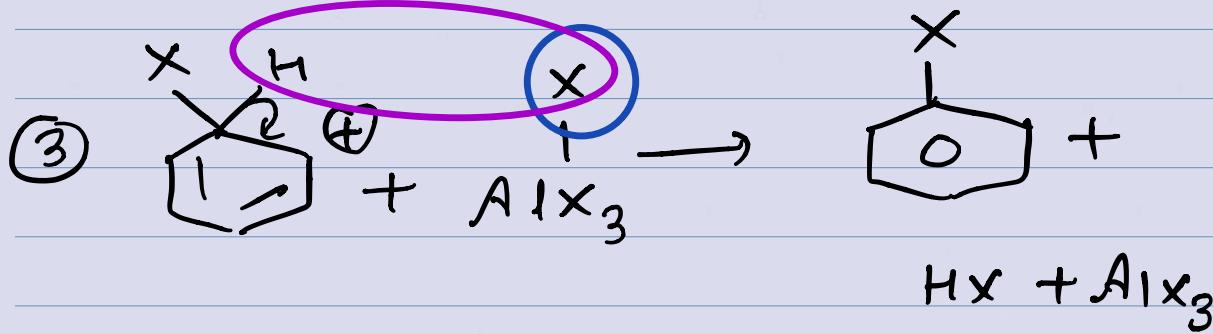
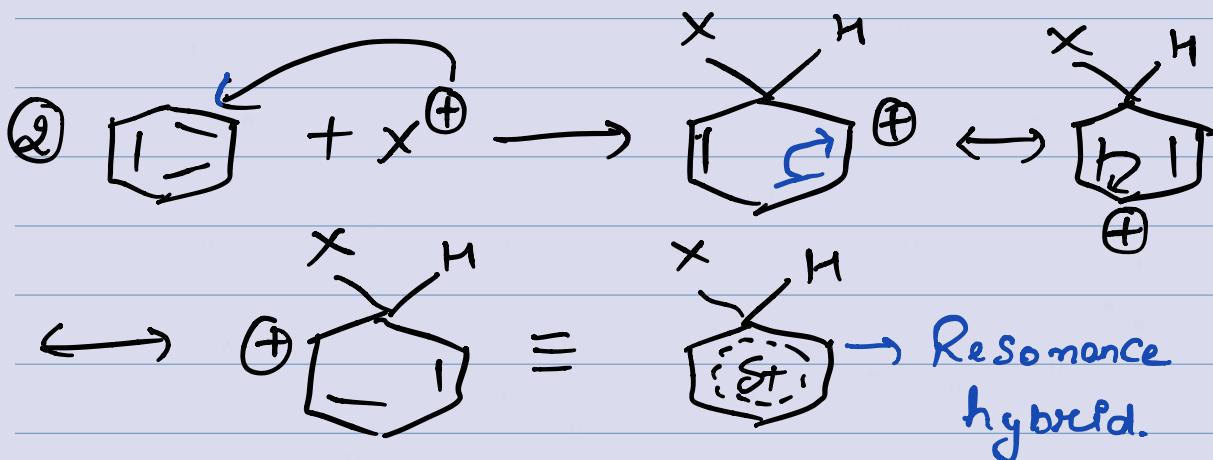
(Aryl halides)

Mechanism

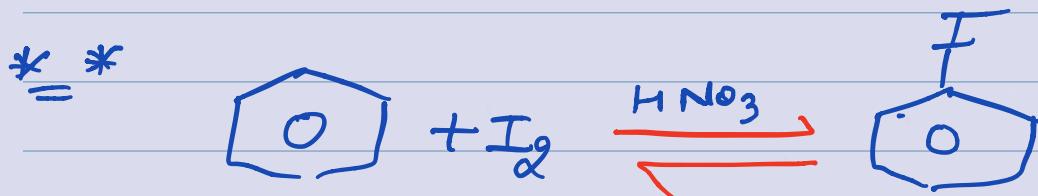
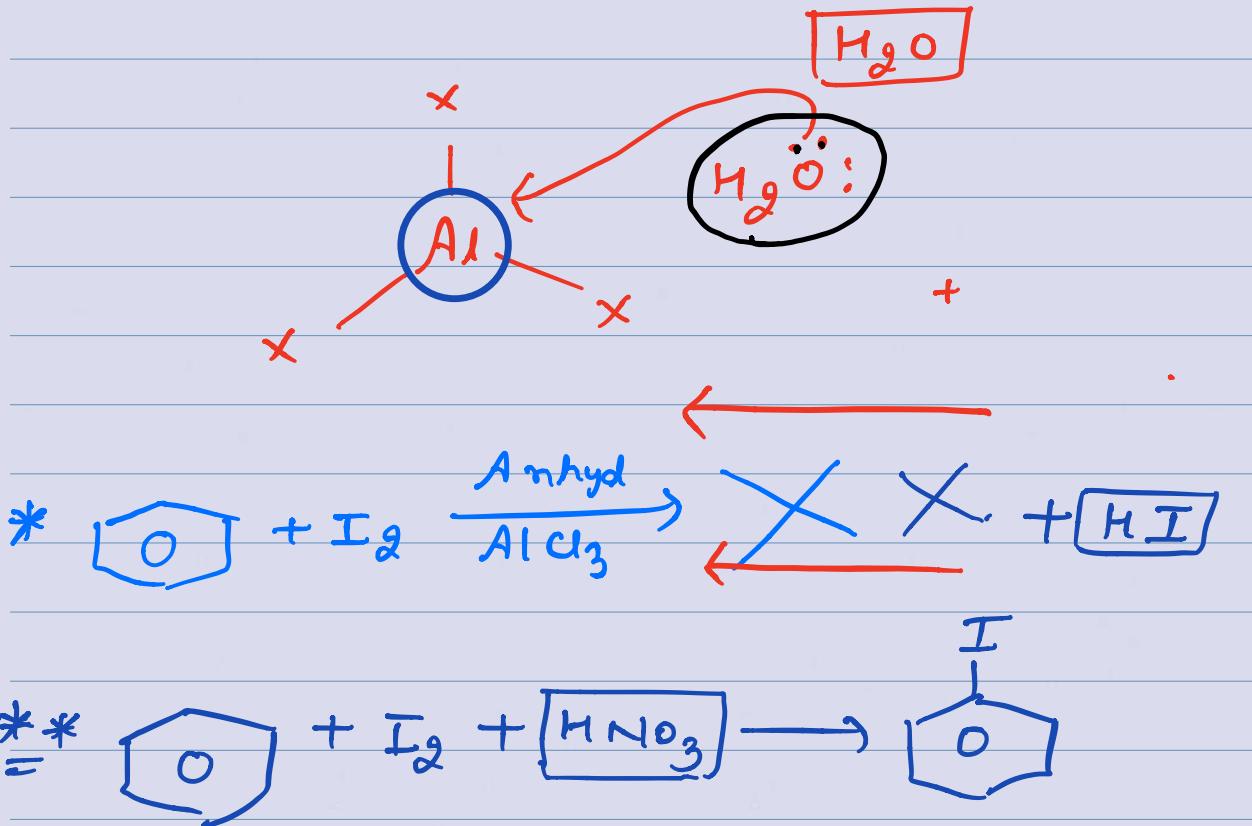
.....



lewis acid . \* Act as an \*  
electrophile.



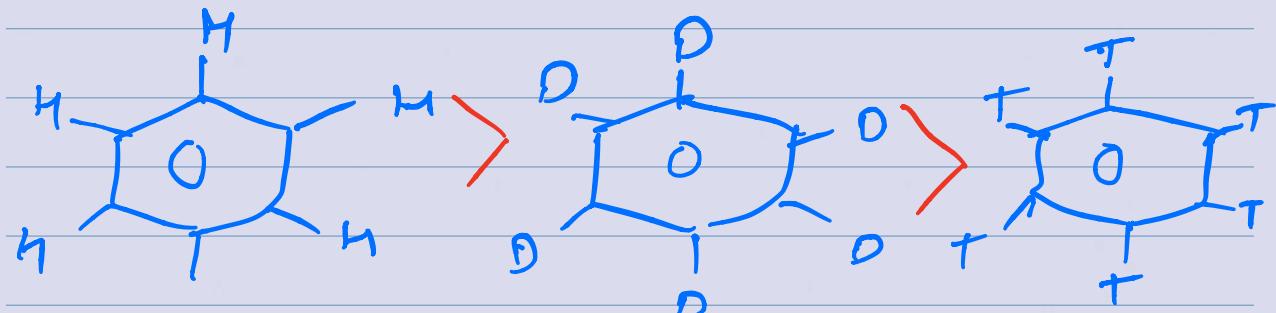
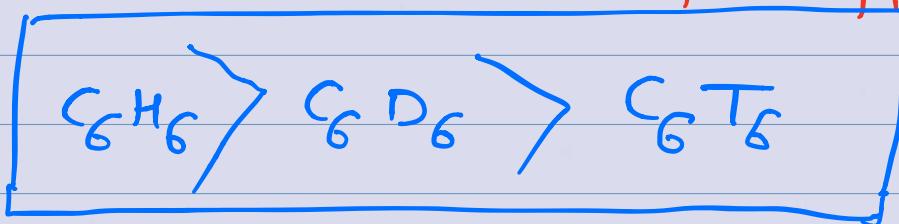
Amhyd  $\text{Al}_x\text{O}_y$   $\Rightarrow$  Hydrous  $\text{Al}_x\text{O}_y$  X.



\* If  $\text{HNO}_3$  will be used then it will oxidise Iodine  $\text{I}^\oplus$  which will behave as electrophile.

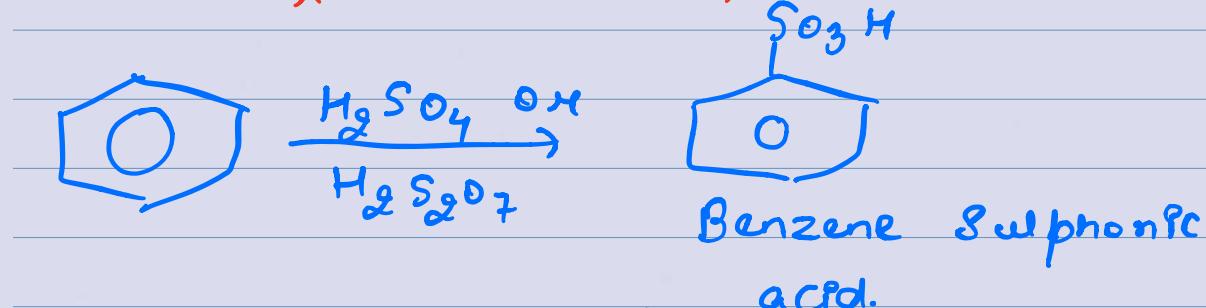
\* Iodination of benzene PS

reversible and hence Pt would  
follows Kinetic Isotopic Effect.



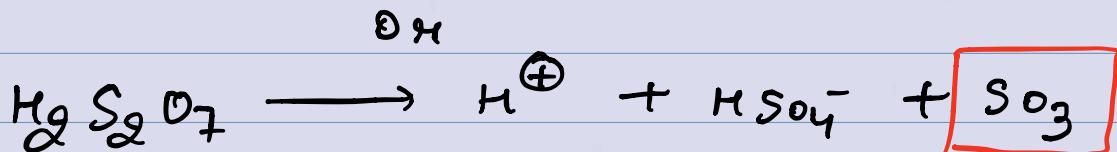
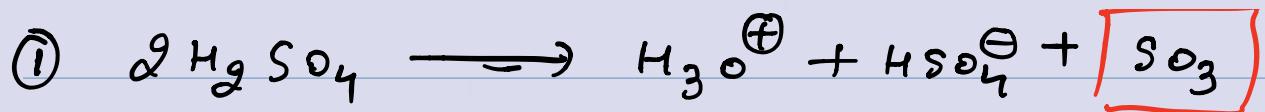
\*\* If an electrophilic substitution rxn of benzene is reversible then Kinetic Isotopic Isotopic effect will be observed.

### # Sulphonation of benzene $\delta^-$



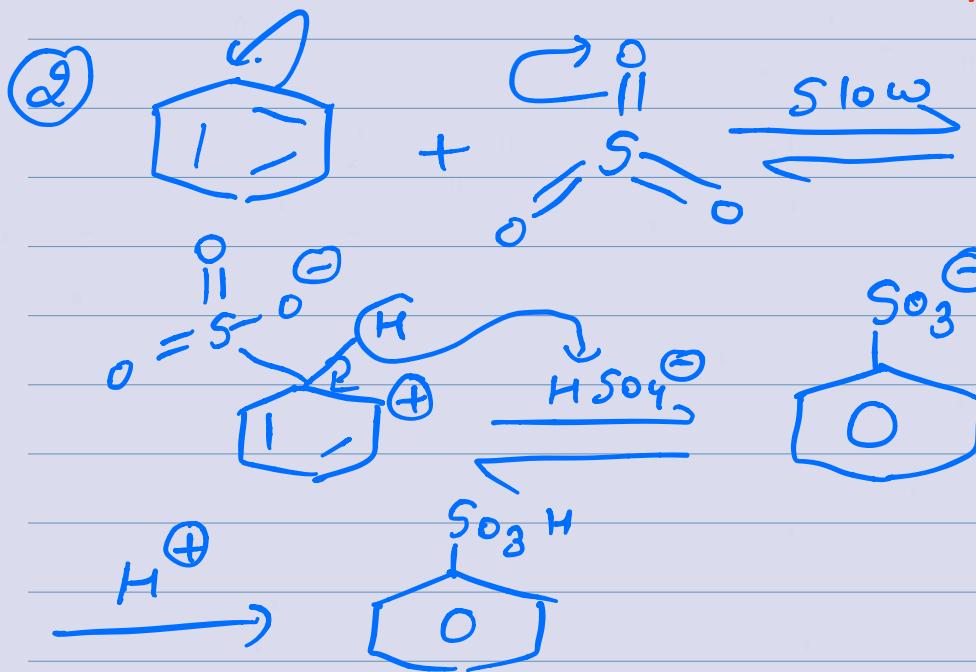
{ Strongest organic acid }

Mechanism :-



$\checkmark \boxed{\text{SO}_3} \Rightarrow \text{No charge}$

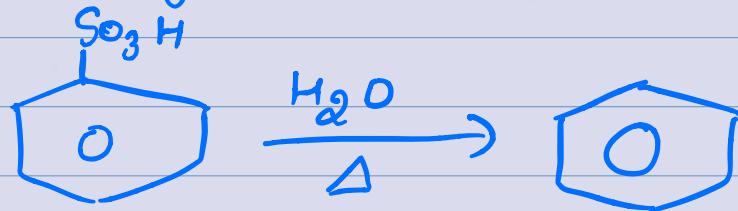
\*\* In sulphonation of benzene neutral  $\text{SO}_3$  behaves as electrophile.



\* Sulphonation of benzene is also reversible and hence it will follow Kinetic Isotopic effect.

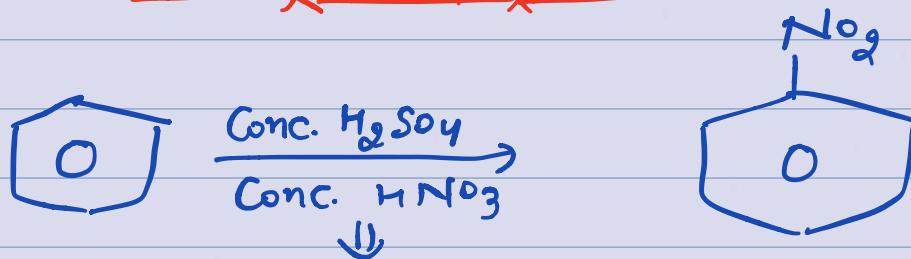
## # Desulphonation :-

\* Desulphonation means removal of  $\text{SO}_3\text{H}$  group.



\* Desulphonation and Sulphonation of benzene are important & utilized to block a particular position.

## # Nitration of benzene :-

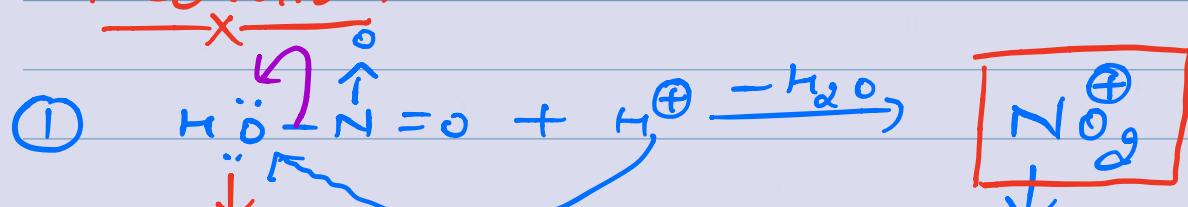


Nitrating mix.

[1 : 1]

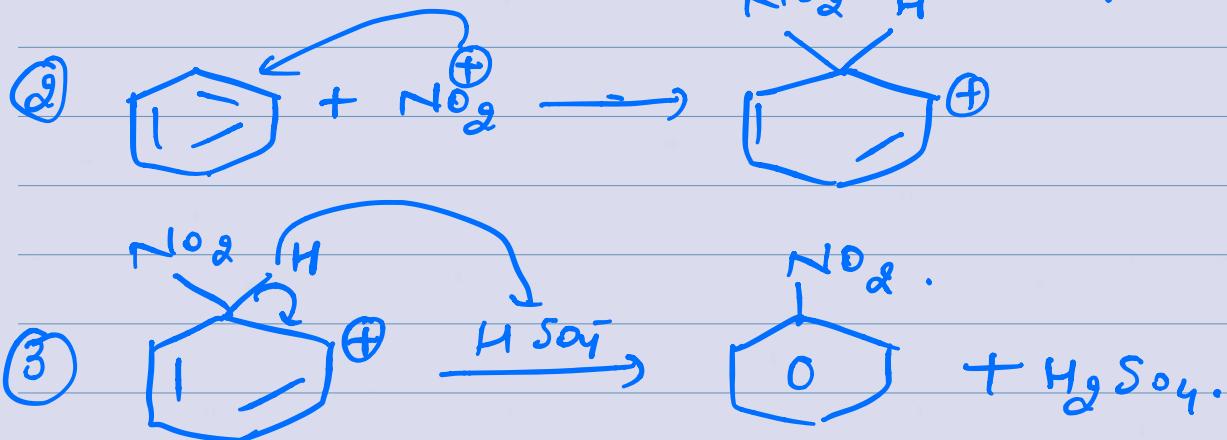
Nitrobenzene.

Mechanism:-



Nitric acid.

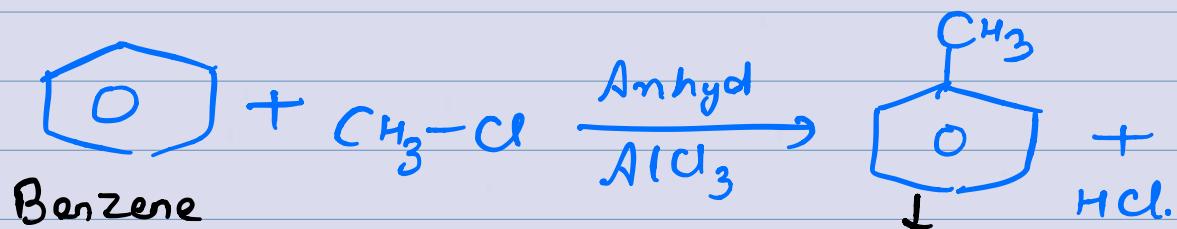
Act as  
electrophile.



# Friedel-Craft's reaction:-

- 1.) Friedel-Craft's alkylation.
- 2.) Friedel-Craft's acylation.

1.) F.C. alkylation :-

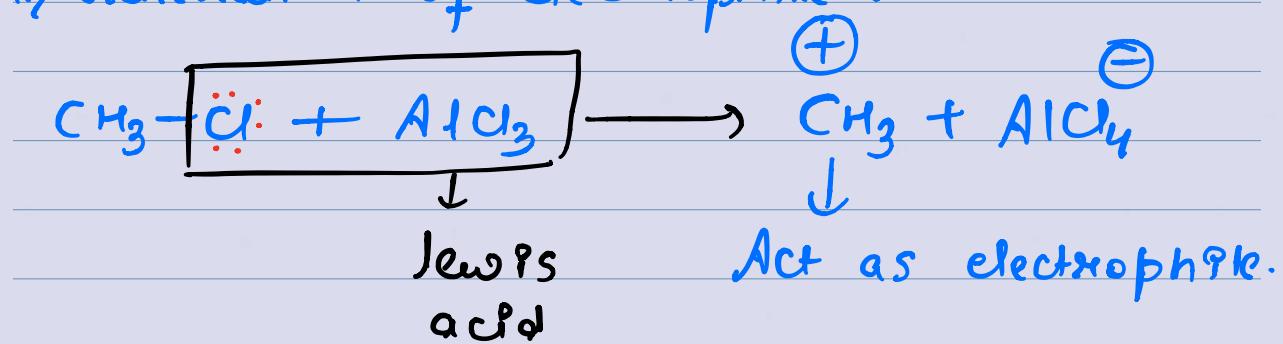


Mechanism

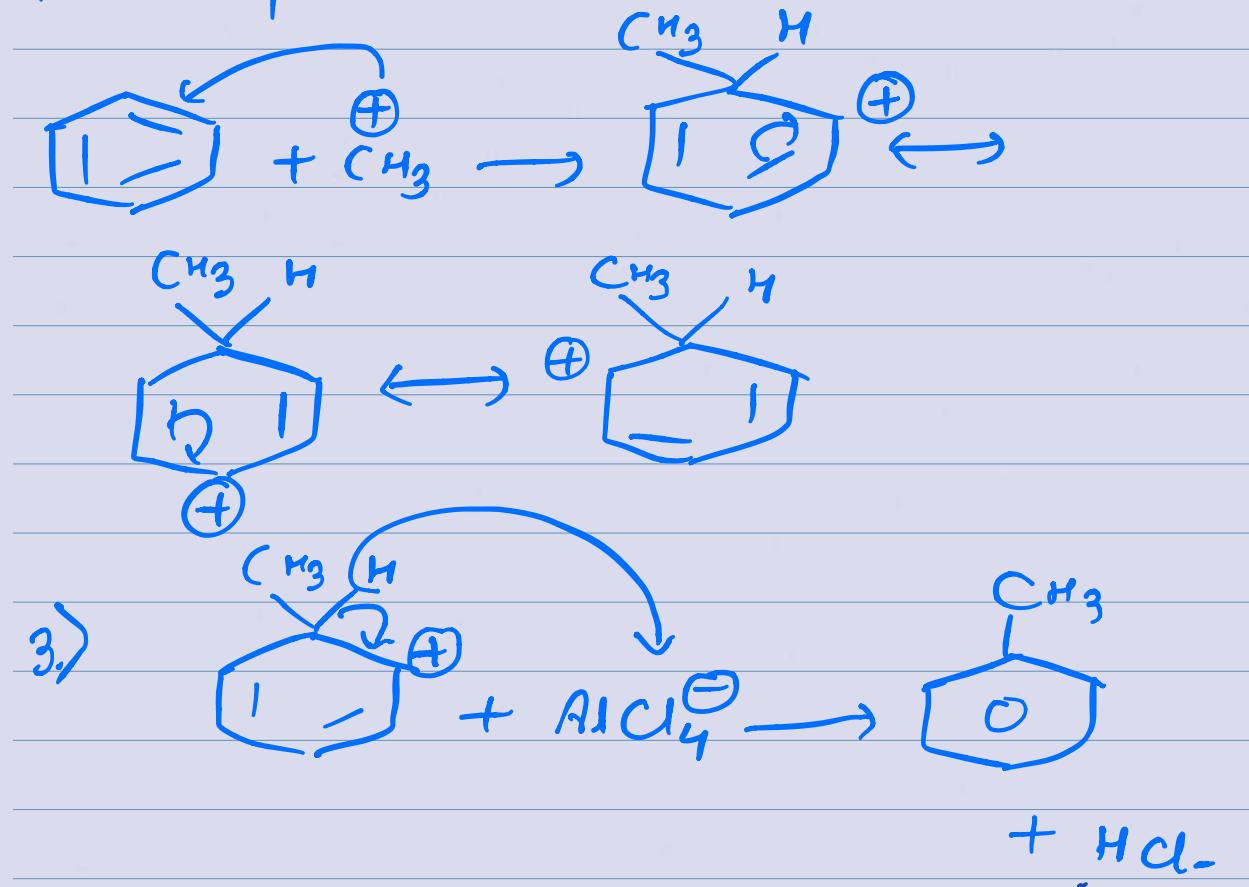
- 1.) Generation of electrophile
- 2.) Electrophilic attack on benzene.

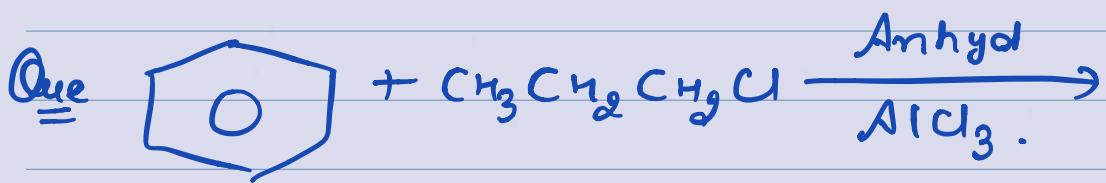
3) loss of protons.

1.) Generation of electrophile  $\overset{\circ}{\text{C}}$ -



2.) Electrophilic attack on benzene  $\overset{\circ}{\text{C}}$ -



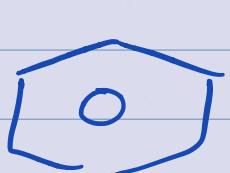


Benzene

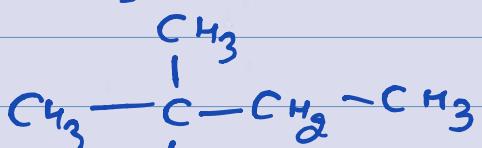
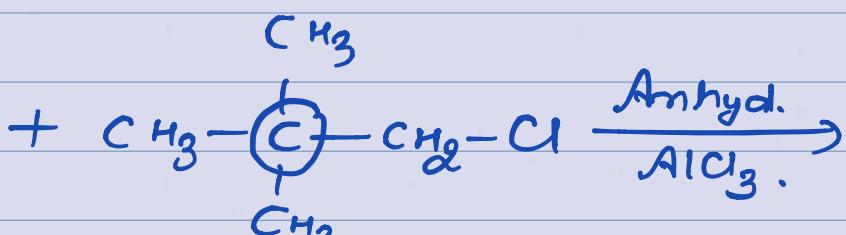


{Cumene?}

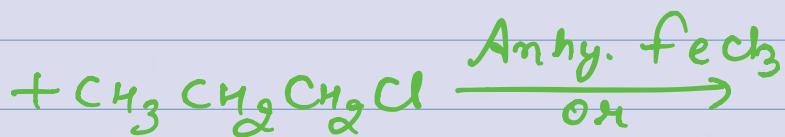
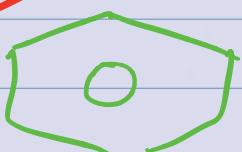
Ques :-



Benzene

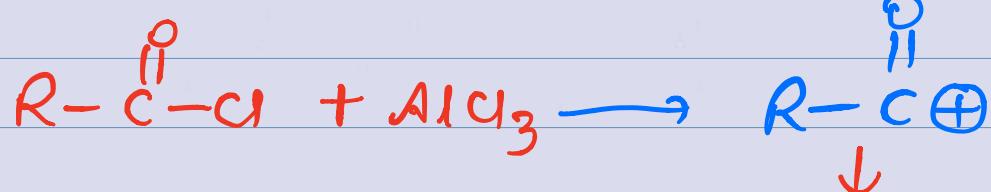
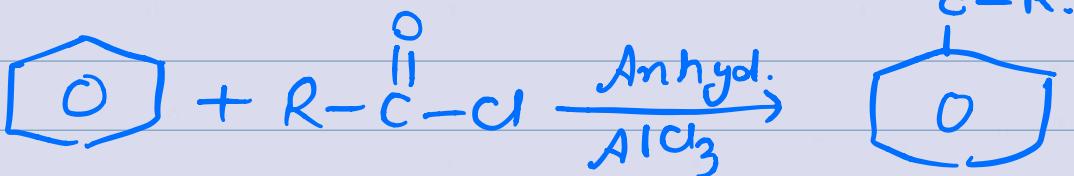
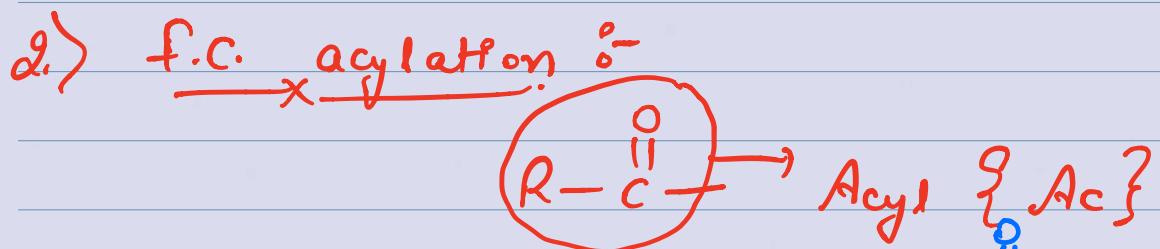
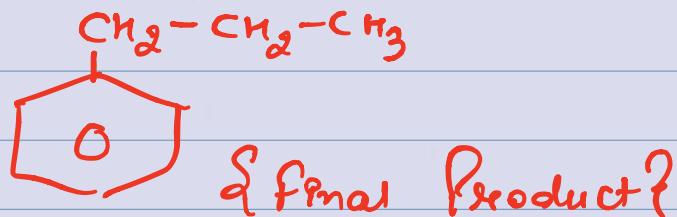


Ques :- 

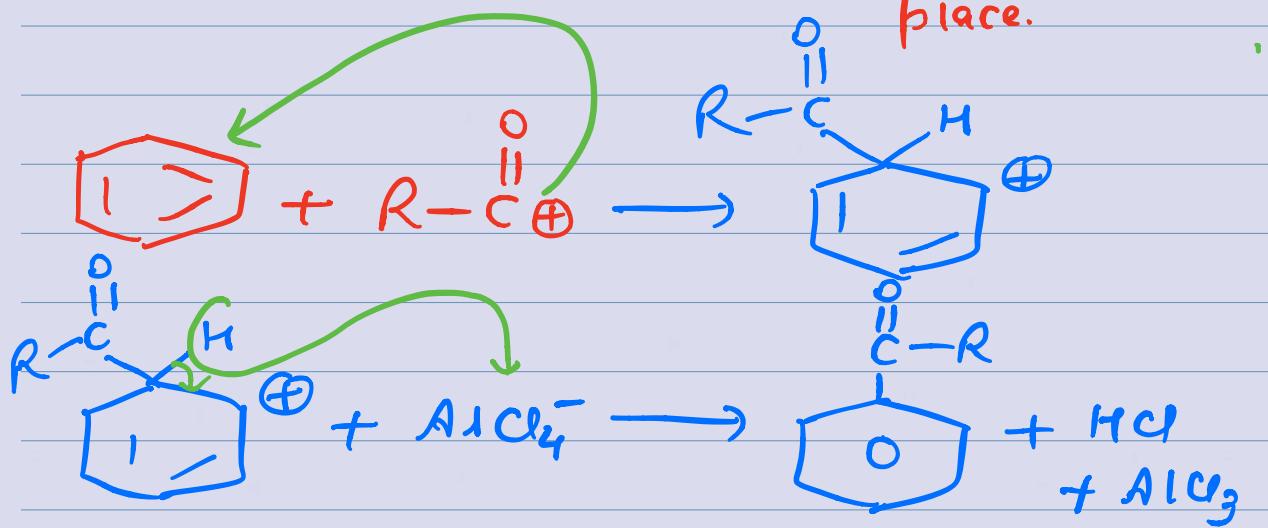


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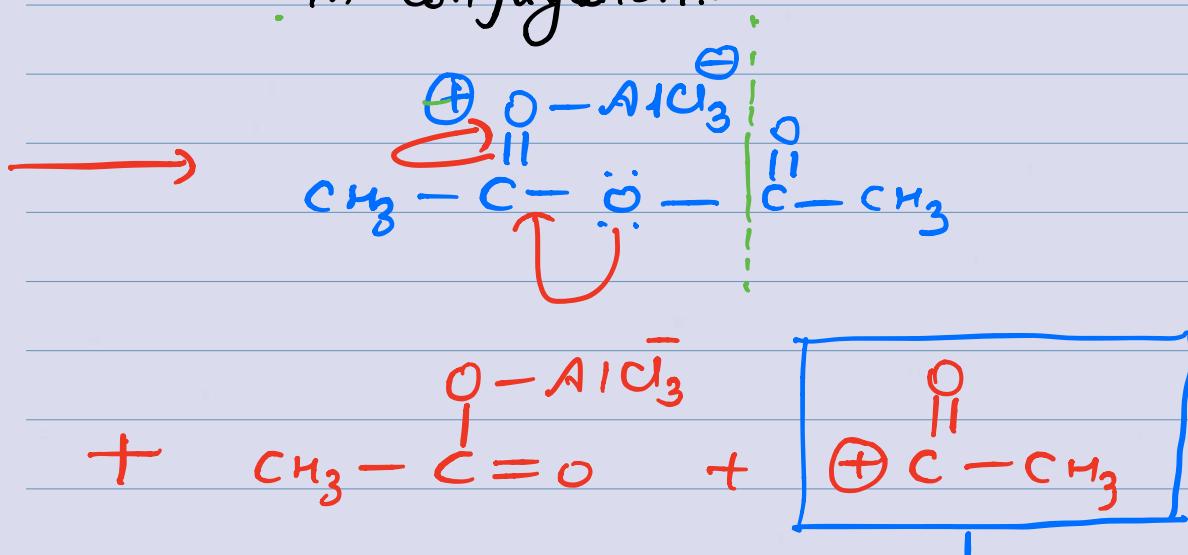
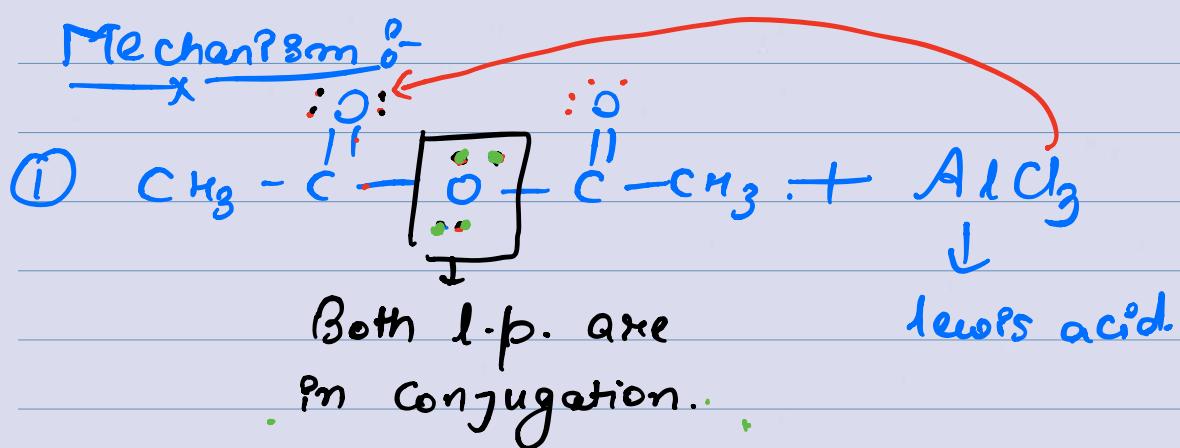
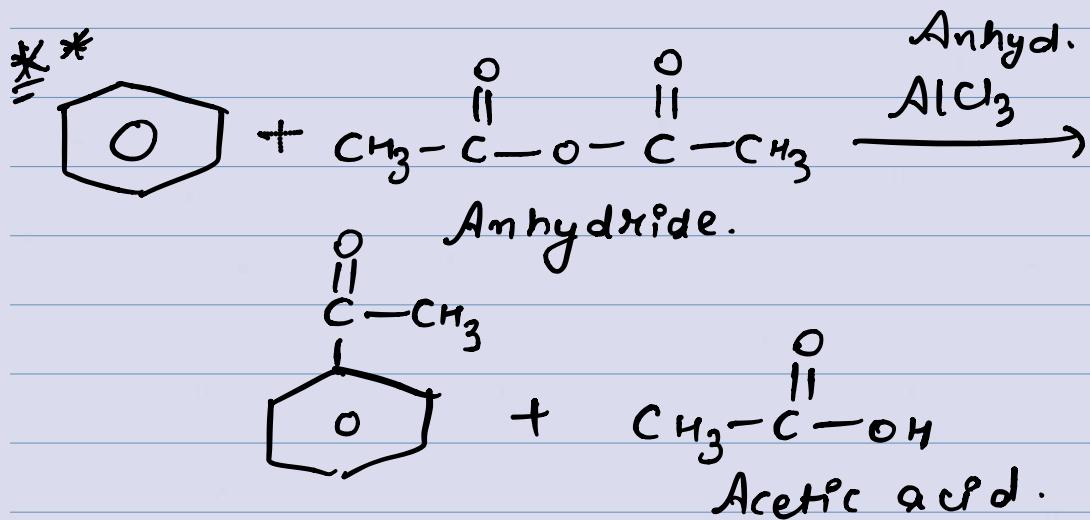
\* No rearrangement  
of carbocation  
takes place.

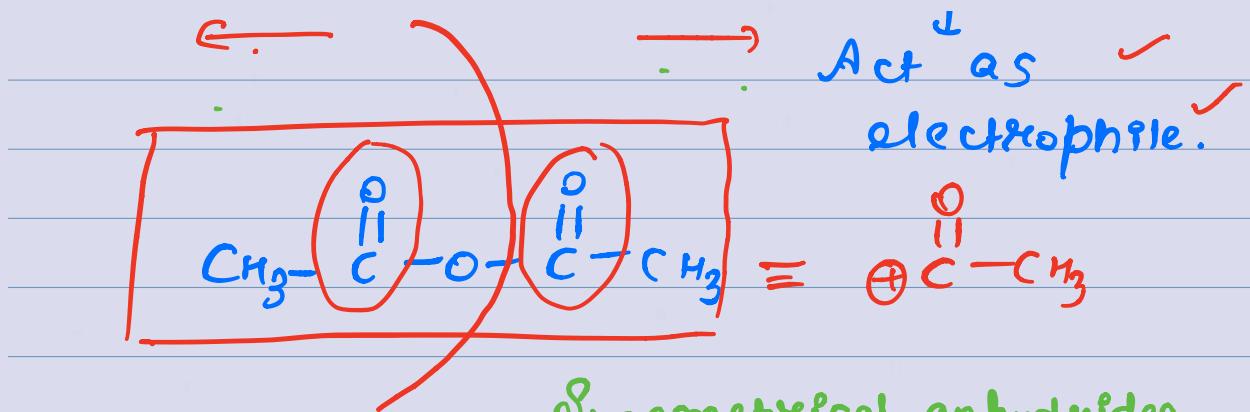


No rearrangement  
with  $\text{AlCl}_3$  takes  
place.

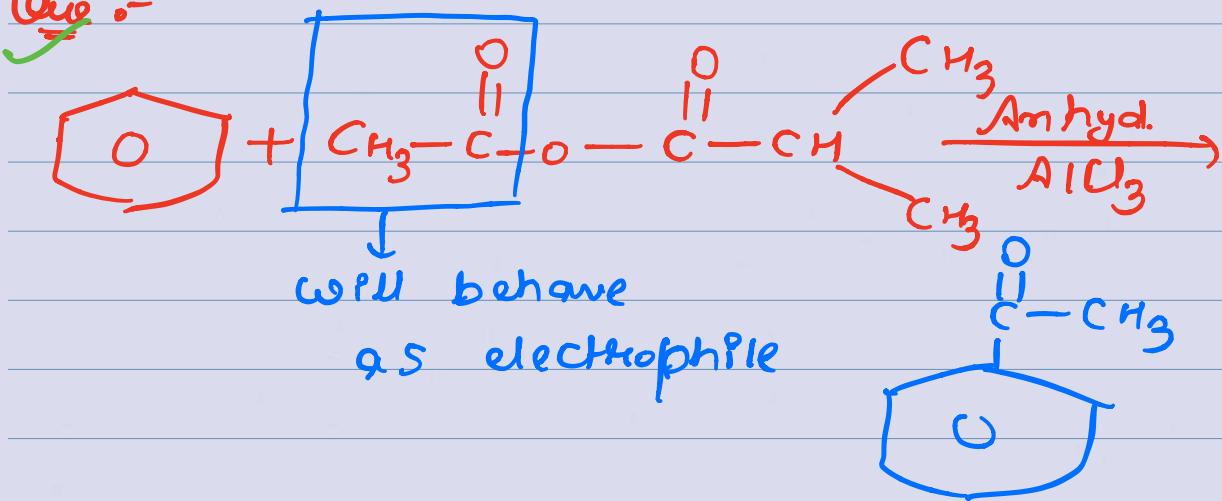


\* for f.c. acylation we can also use anhydrides.





Ques :-



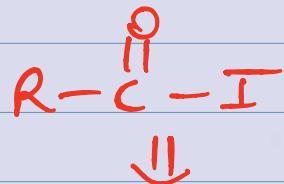
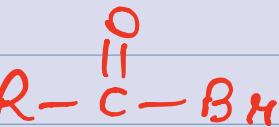
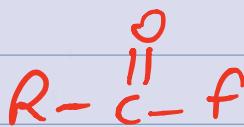
\* In case of unsymmetrical anhydrides, less steric hindered acyl group will behave as electrophile.

Ques :- R-F R-Cl R-Br R-I

$\Downarrow$

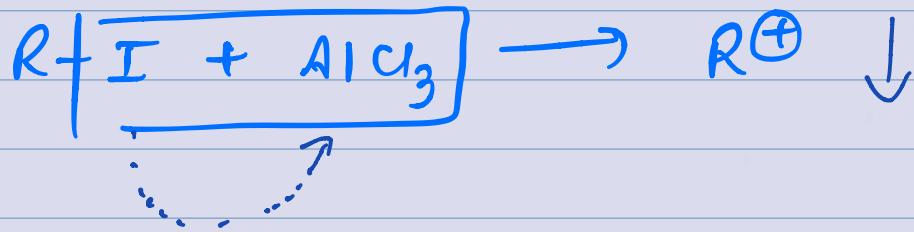
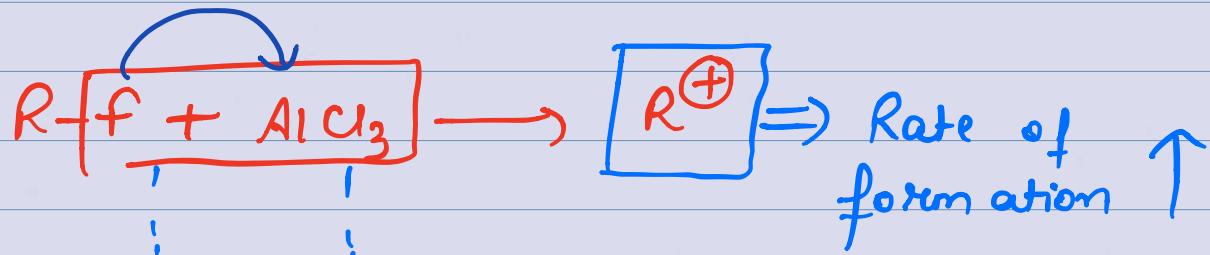
Compare the rate of f.c.  
alkylation.

Ques :-



Compare rate of f.c. acylation.

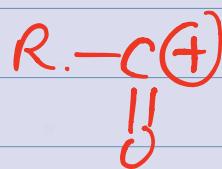
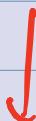
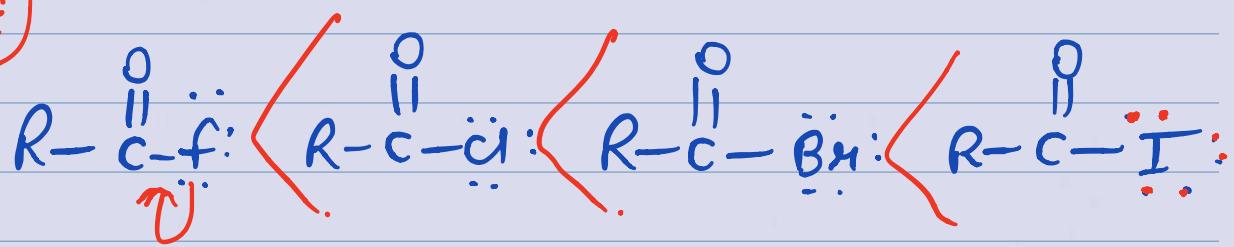
①



\* In case of alkylation the 1<sup>st</sup> step is formation of carbocation which has been formed, when halogen atom has coordinated its e<sup>-</sup> pair with AlCl<sub>3</sub>

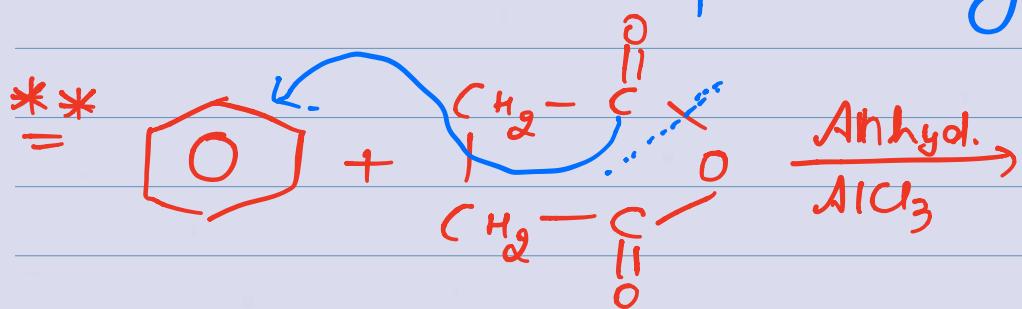
\* Due to very small size of f. p.t.s tendency to coordinate e- pair will be highest and hence Rate of f.c. alkylation will be maximum.

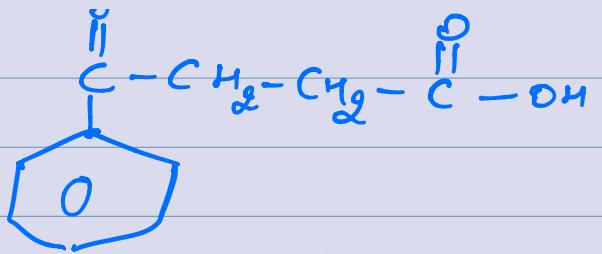
(2)



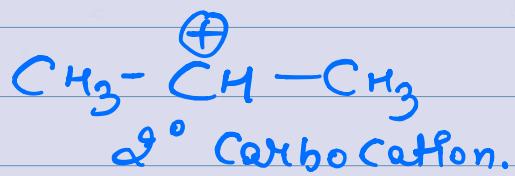
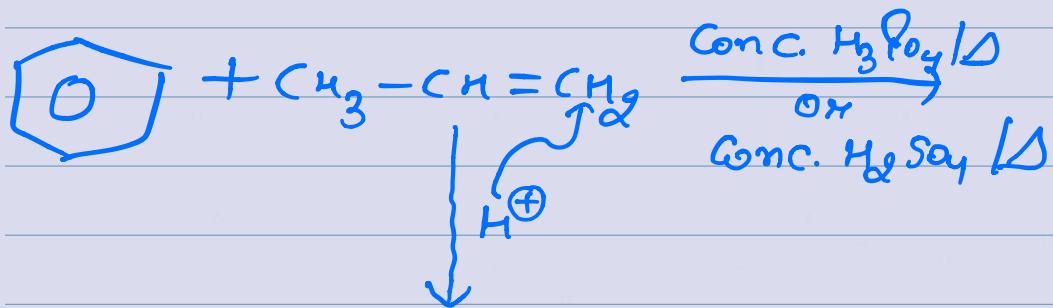
\* L.P. of halogens are in conjugation

\* Hence due to very small size of fluorine p.t.s tendency to acquire partial double bond character will be max<sup>n</sup> and hence lesser will be rate of f.c. acylation.

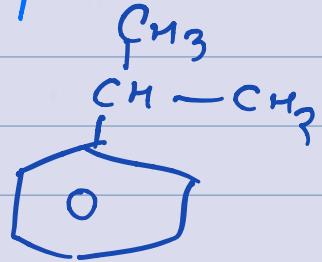




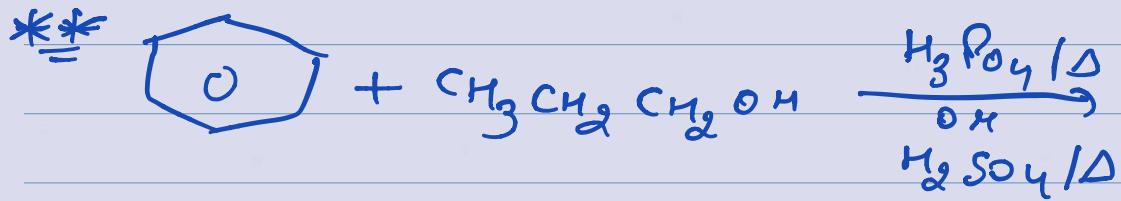
# Some other alkylating reagents:-



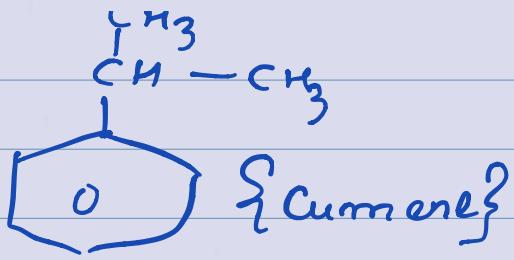
Behave as an electrophile.



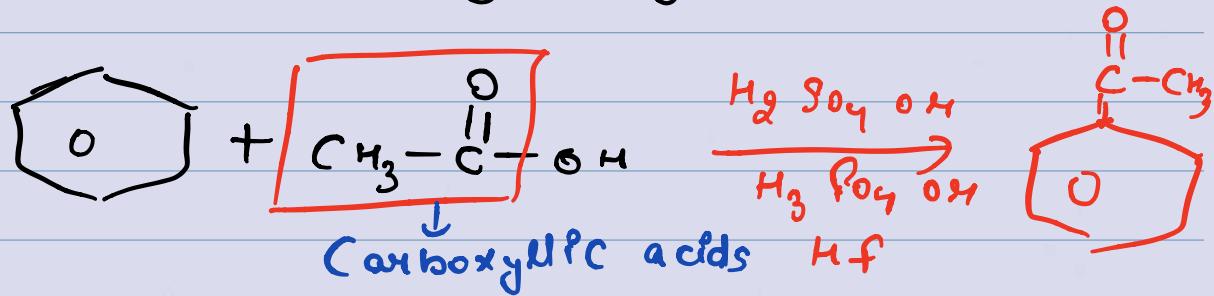
Cumene.



c.



⇒ Other acylating reagents:-



# Limitations of Friedel-Craft's reaction :-

Activator → Increases  $e^- \uparrow$

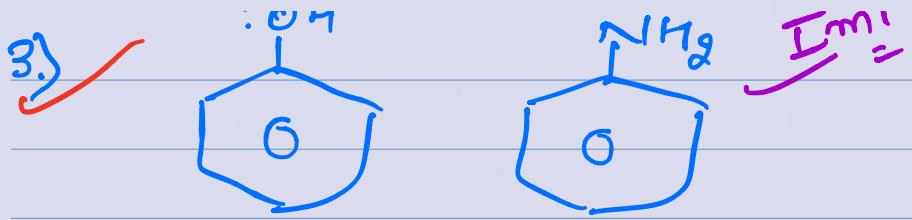
1.) Benzene and activator compounds gives Friedel-Craft's alkylation as well as acylation.

2.) All deactivator compounds do not give Friedel-Craft's alkylation as well as acylation.

∴

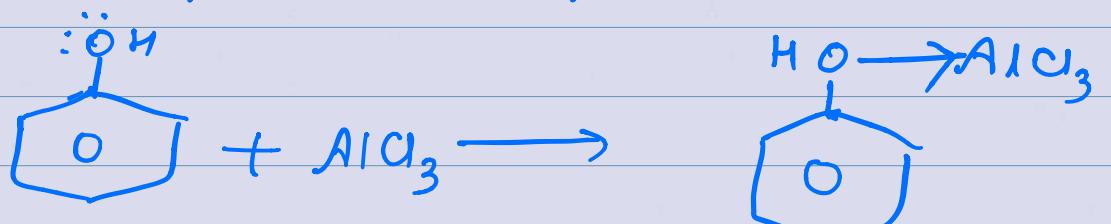
..

?

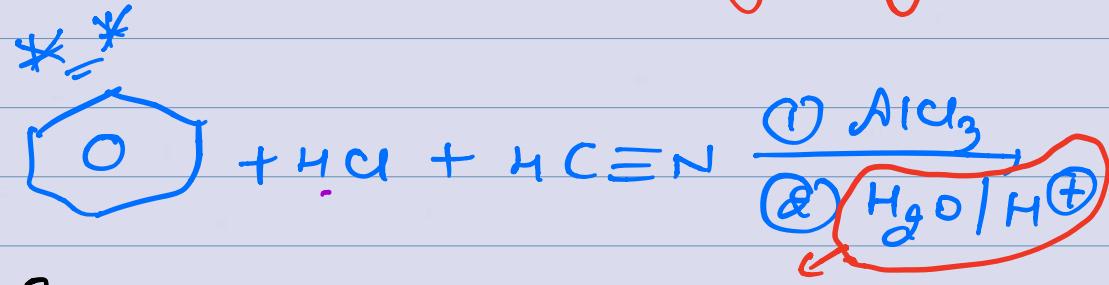


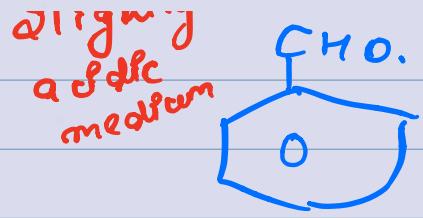
\* Although  $-OH$  and  $-NH_2$  group are strong activators, they do not give f.c. alkylation as well as f.c. acylation.

\* Because both Phenol and aniline react with  $AlCl_3$  and form a complex.



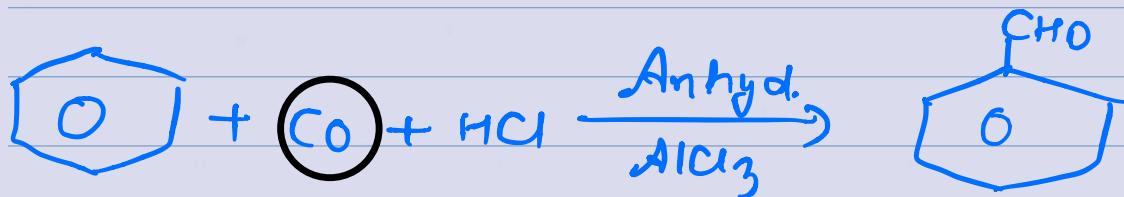
## # Grignard Aldehyde Synthesis :-



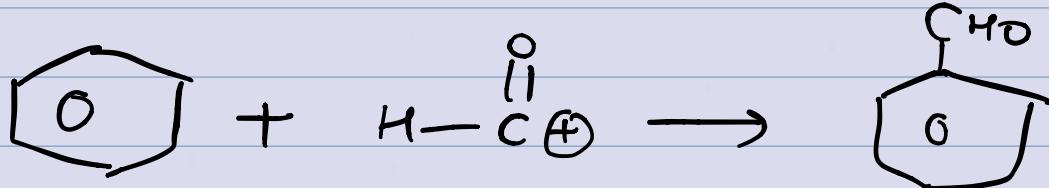
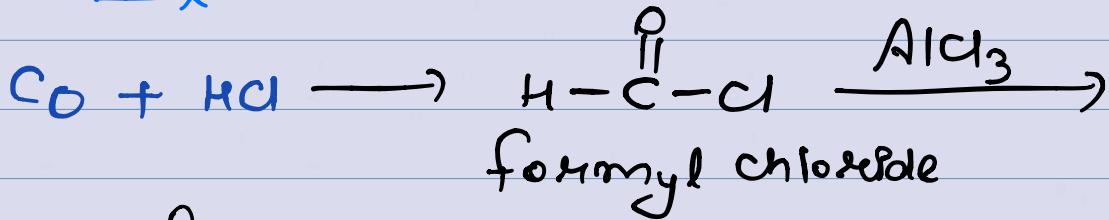


Benzaldehyde.

# Grattermann Koch Synthesis  $\delta^-$

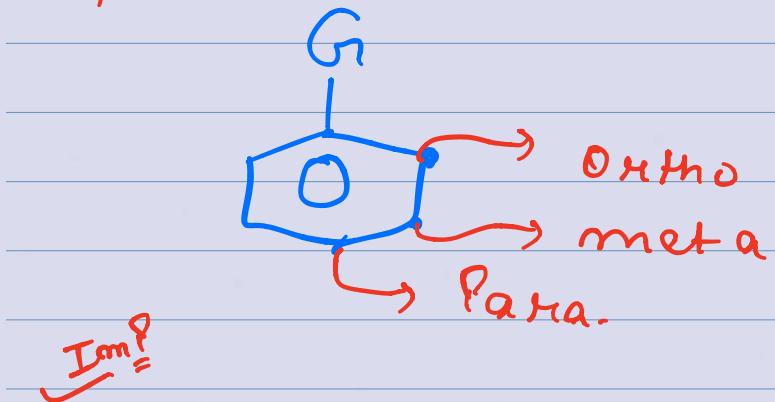


Mechanism

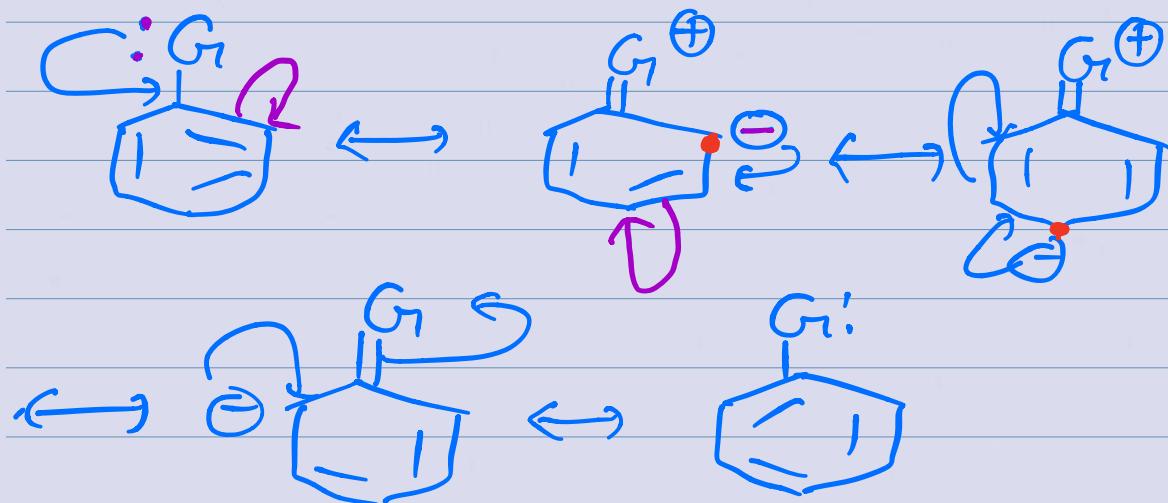


Koch  $\rightarrow$  CO + HCl.

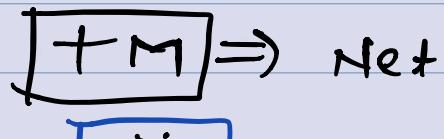
## # Electrophilic Substitution rens of Substituted benzene :-

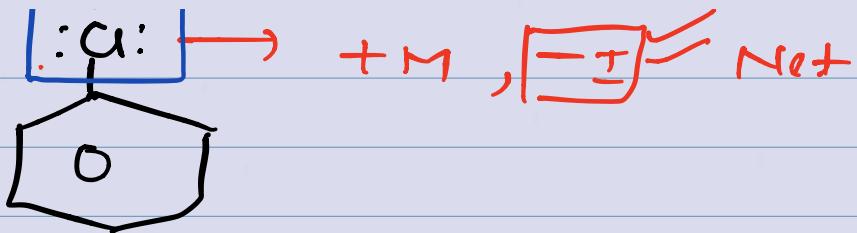


\* \* Activators & Deactivators :-

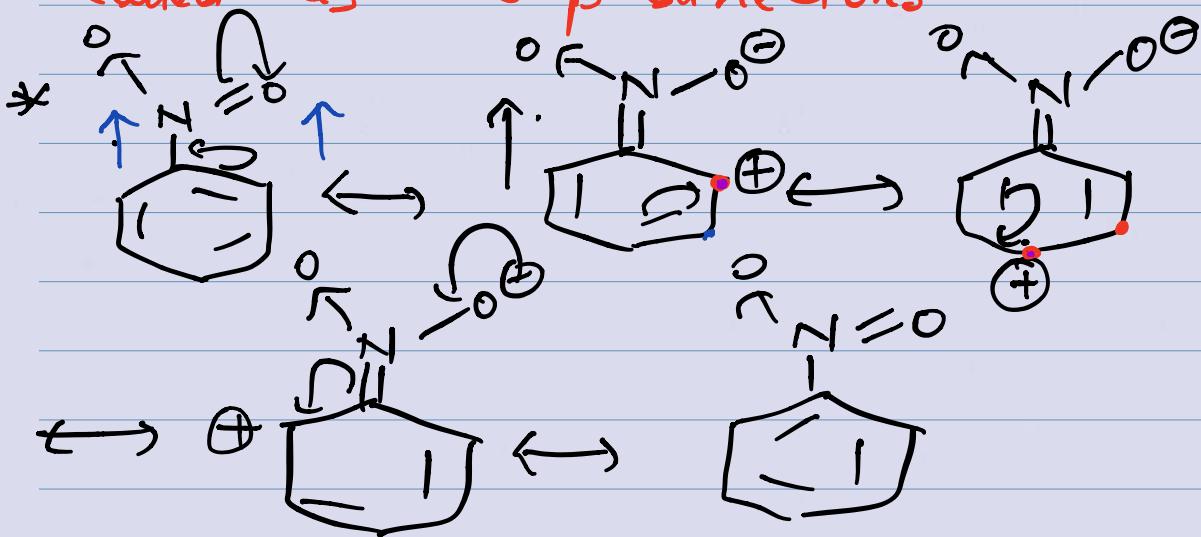


\* The groups which increases the e- density of the benzene being Due to  $+M$  or hyperconjugation ( $+H$ ) are known as activators



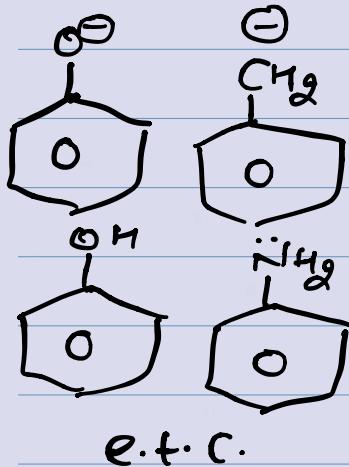


\* The groups which shows +M effect (Resultant) increases the e- density of the ring and especially at ortho and para positions. Such groups are also called as O-p directors.

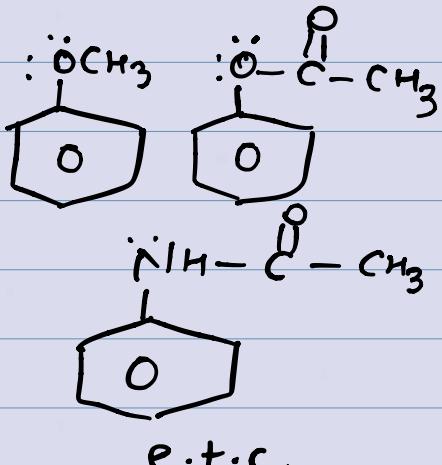


\*\* The groups which decreases the e- density of the ring due to -M, -H & -I are known as deactivators. and also known as meta directors.

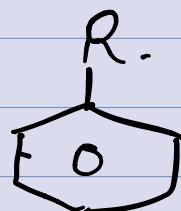
### Strong Activators



### Moderate Activators

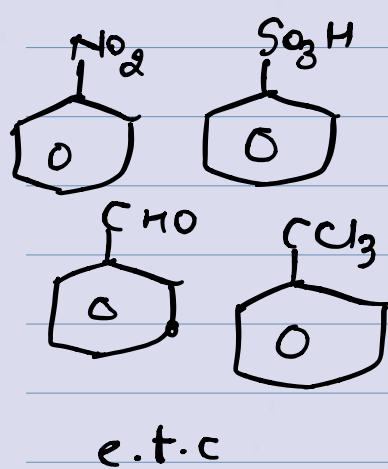


### Weak Activators

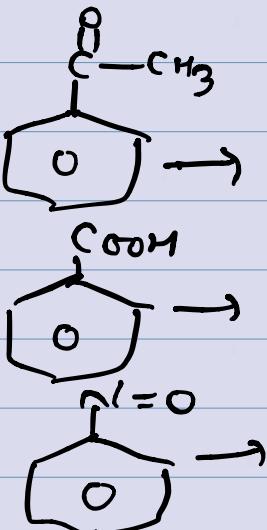


e.t.c.

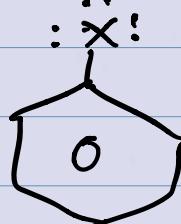
### Strong Deactivators



### Moderate Deactivators

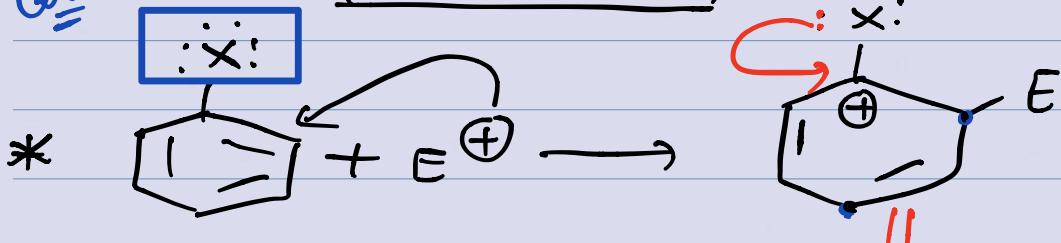


### Weak Deactivators



Halo benzene

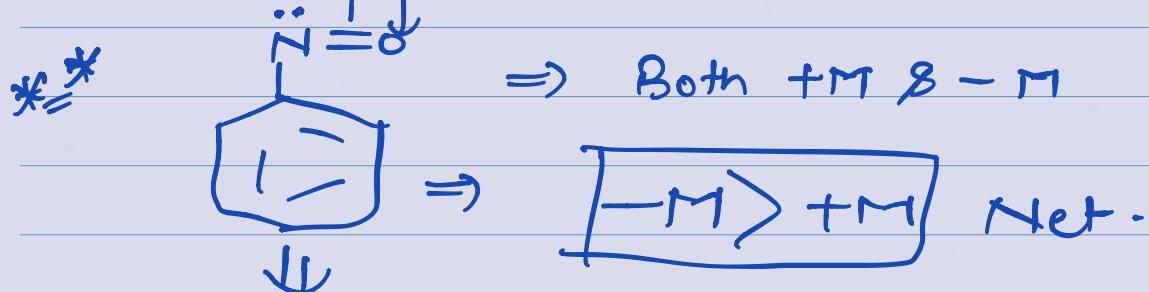
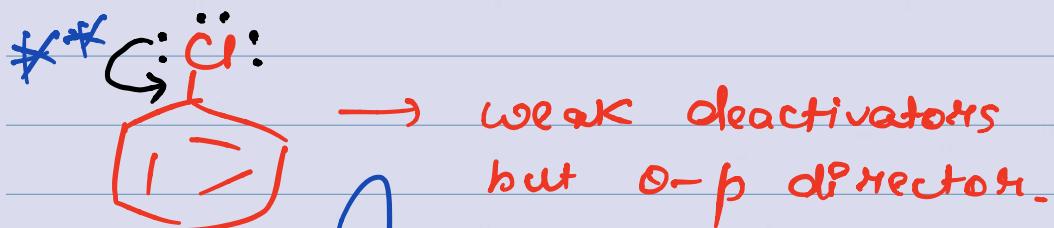
$\text{Q}_{\text{de}}^{\text{2}}$



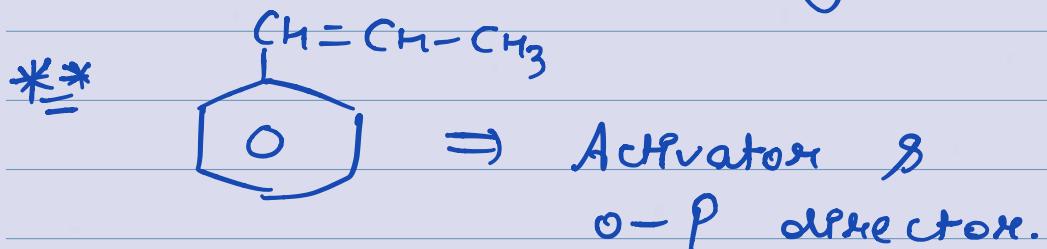
1)

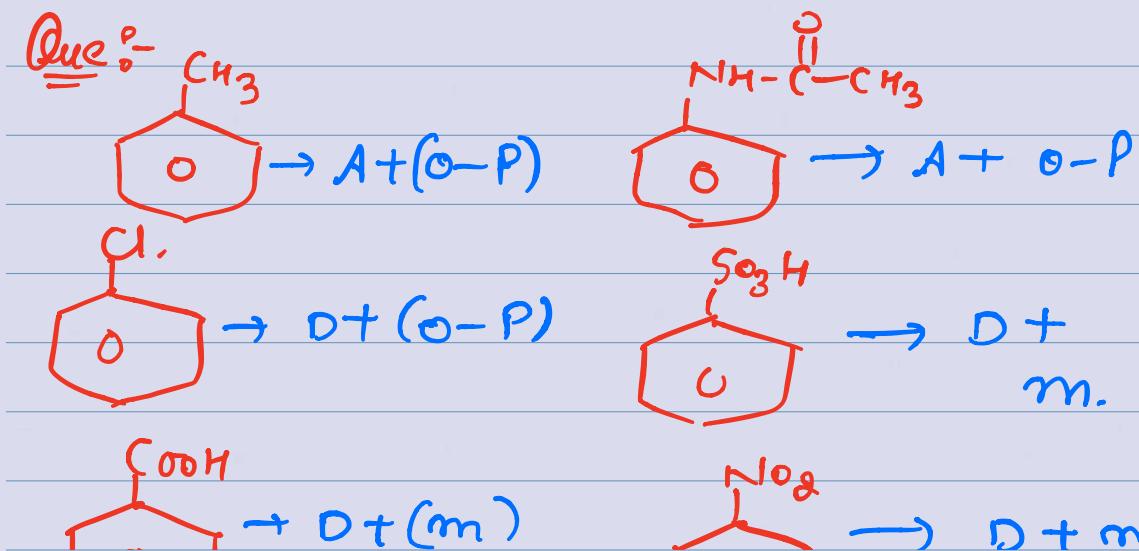
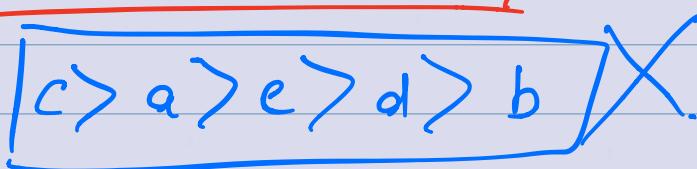
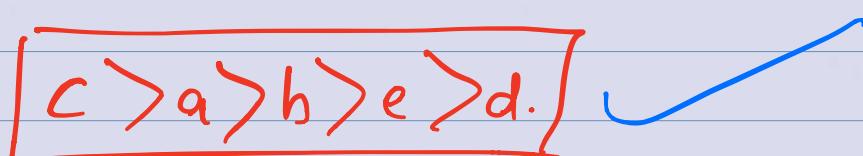
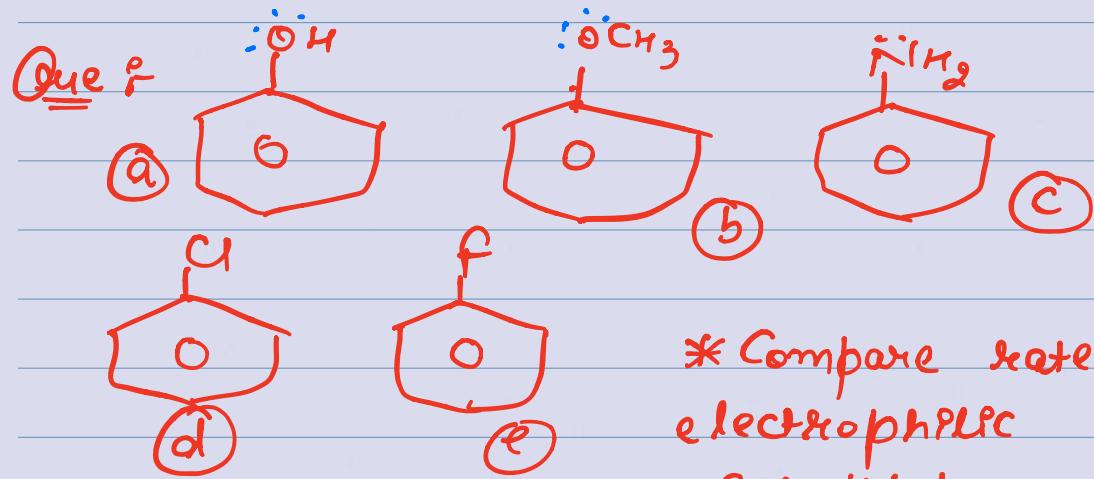
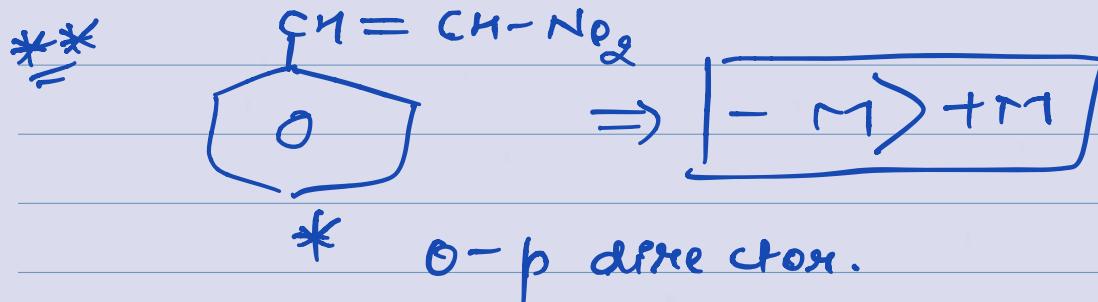
Stabilized by  
back bonding.

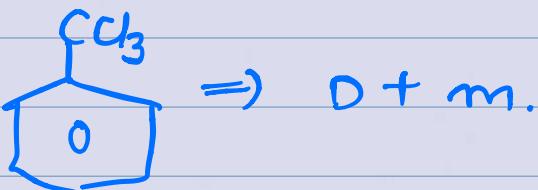
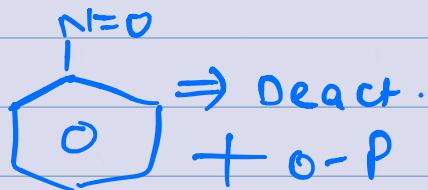
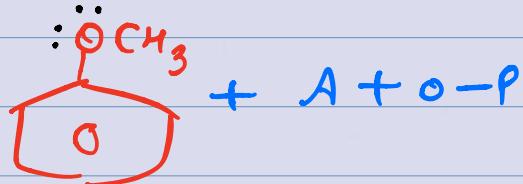
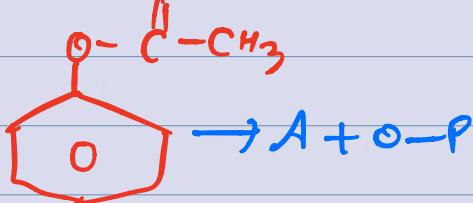
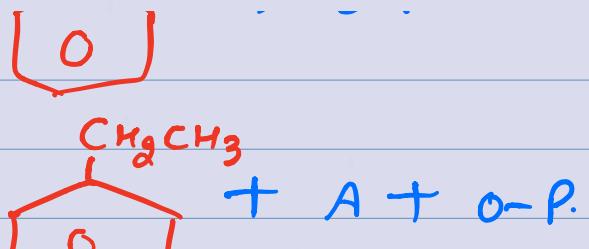
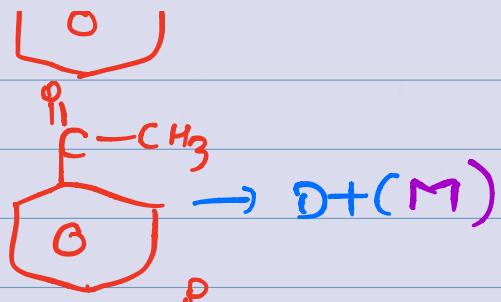
- \* The groups which have tendency to show +M effect { Resultant doesn't matter } they are always O-P directors



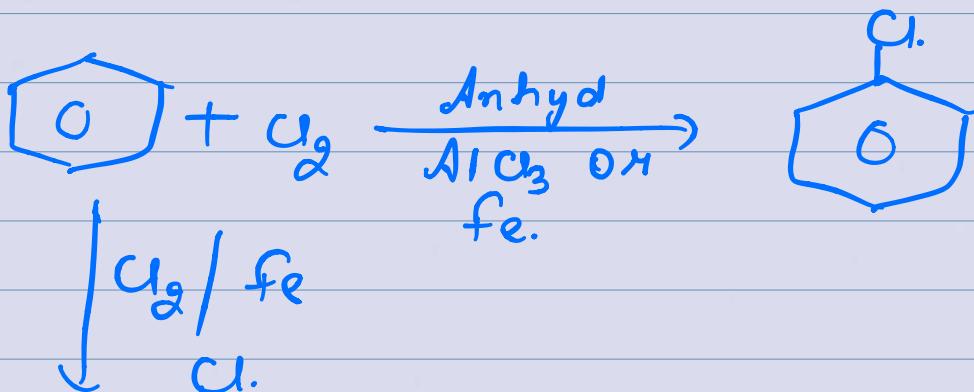
If will be a deactor but  
Yet O-p directing in nature.



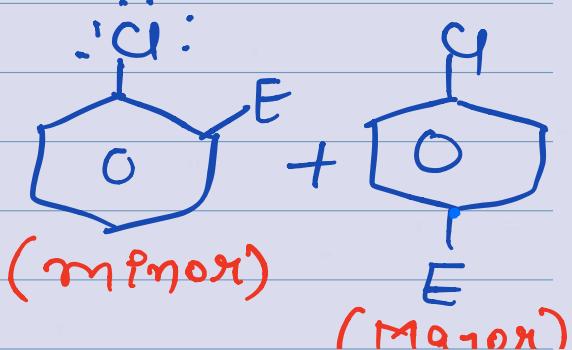
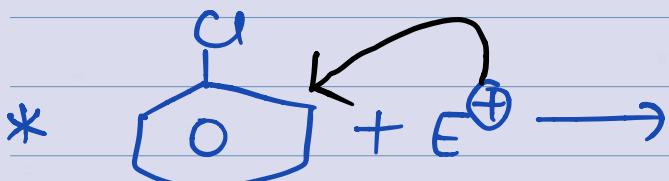
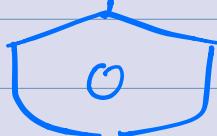




# Chlorobenzene or halo benzene :-



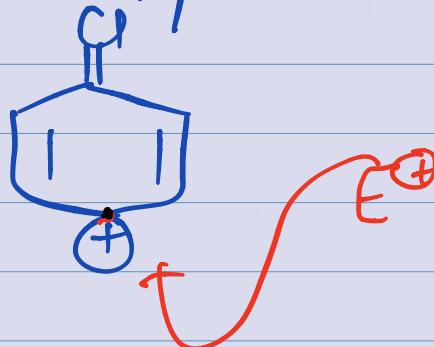
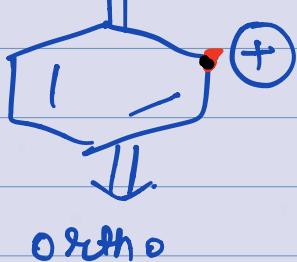
$\downarrow \text{Cl}_2 / \text{fe}$



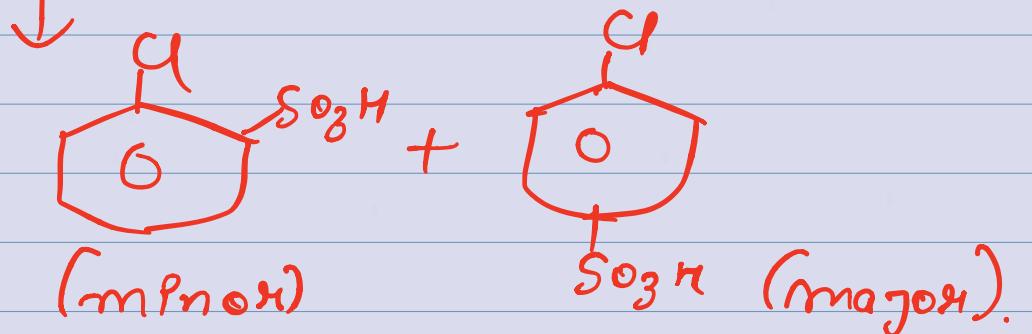
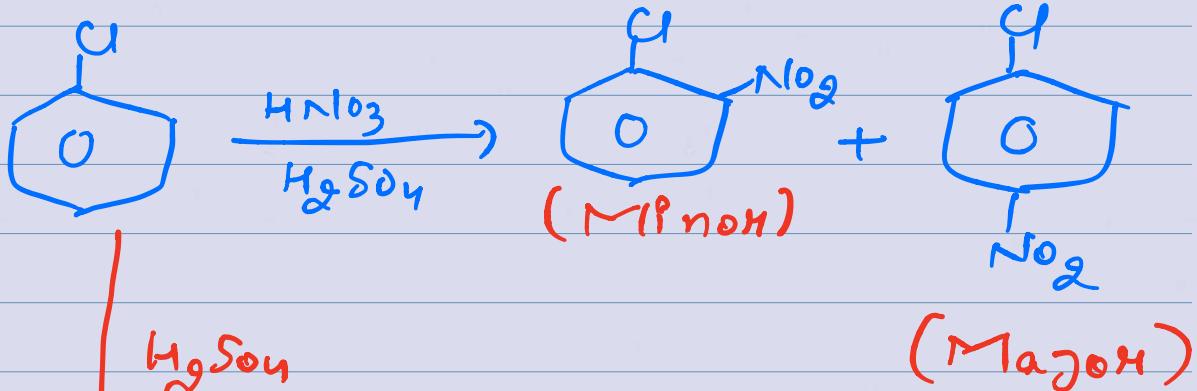
$+M \rightarrow$  Distance independent.

$-I \rightarrow$  Distance dependent.

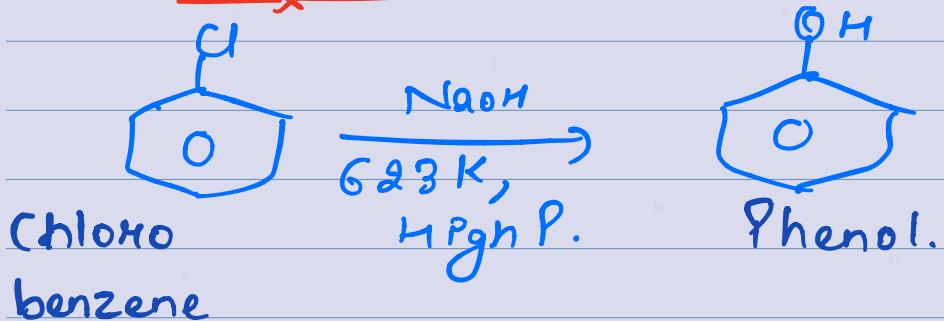
Cl:



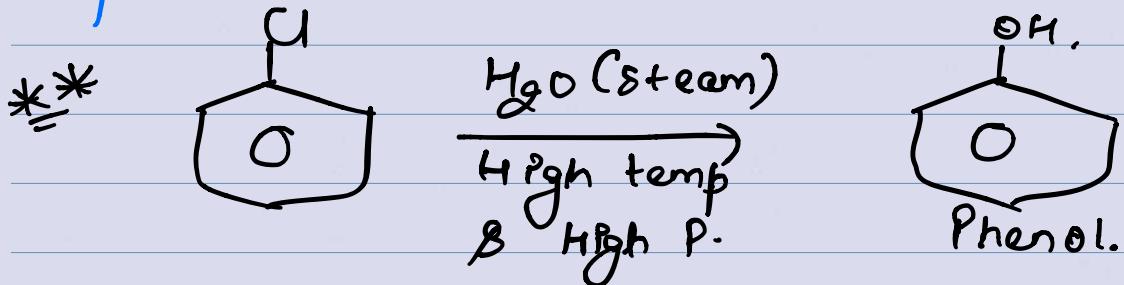
\* Nitration of chlorobenzene



## # Dow's Process

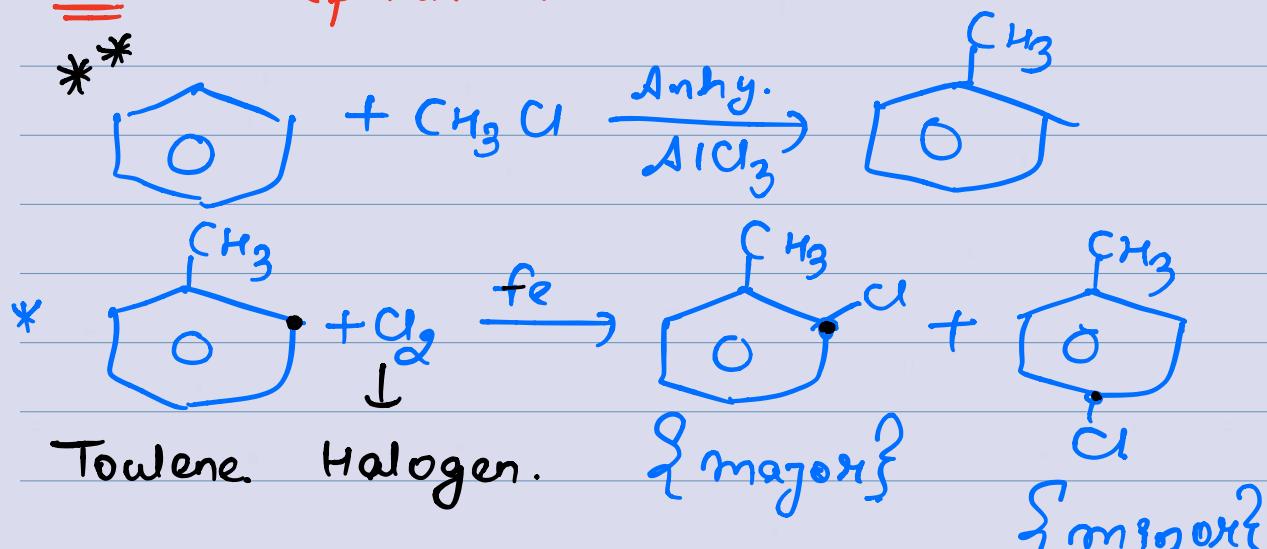


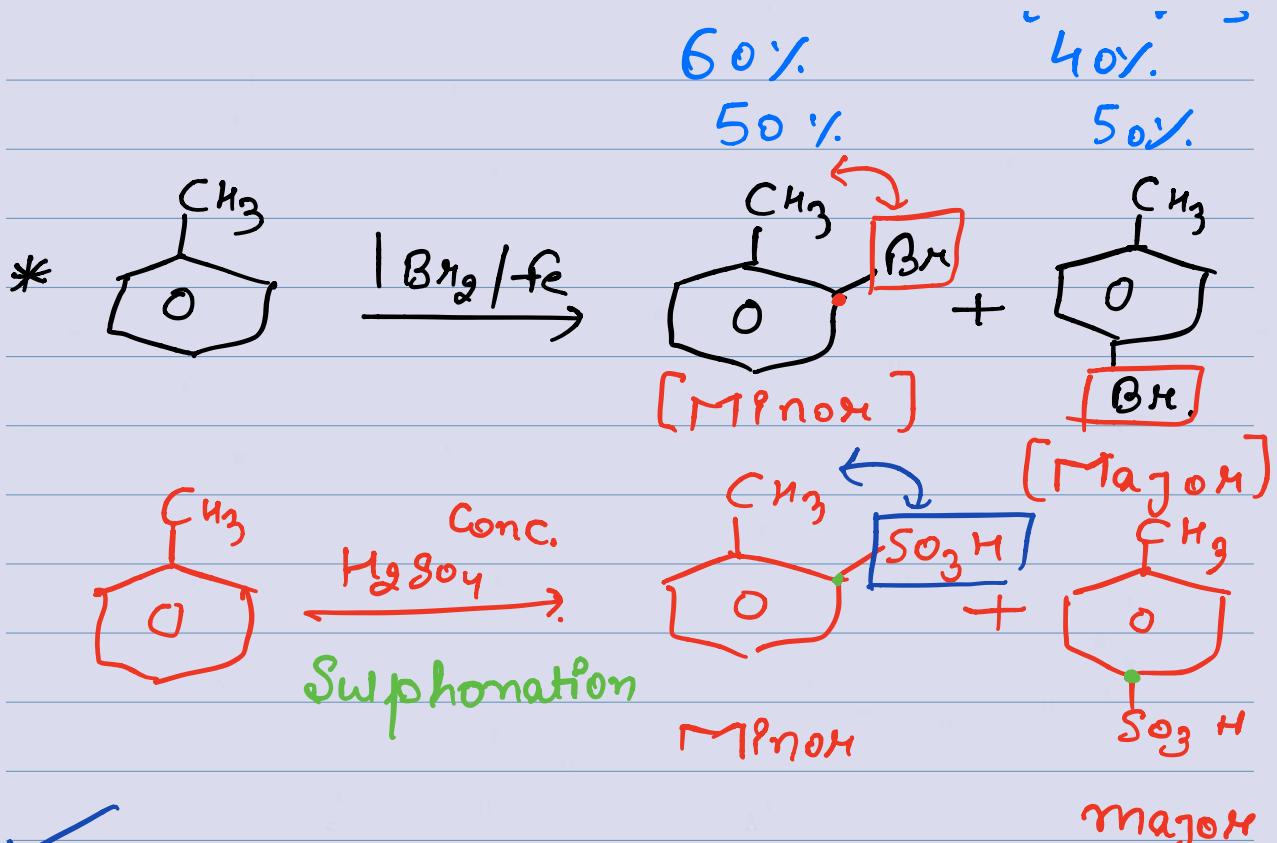
- \* Conditions are normal  $\Rightarrow S\text{N}^2$  X
- \* In Dow's process chlorobenzene follows  $S\text{N}^2$  mech<sup>n</sup>.



## # Toulene

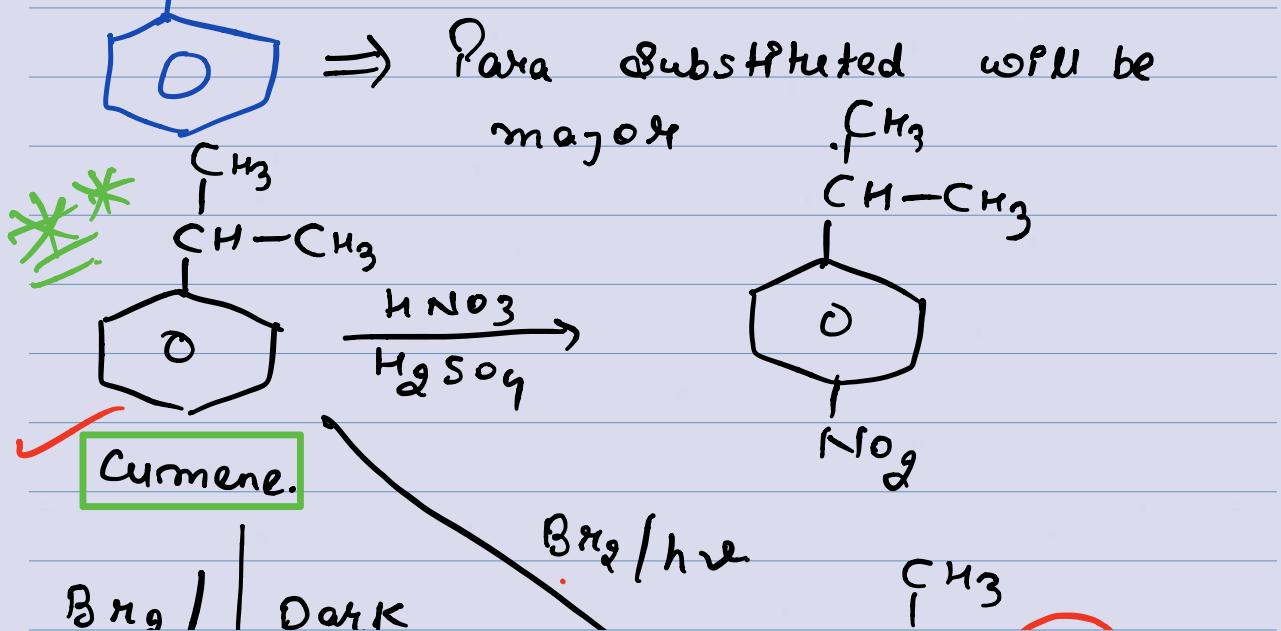
### Preparation:

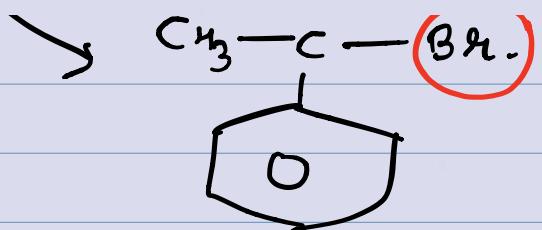
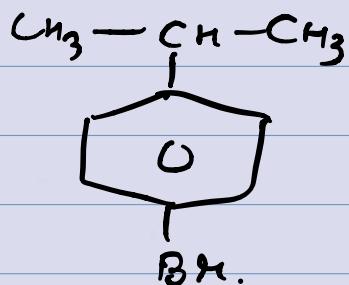
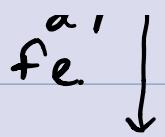




\* Para sub. is major due to less steric hindrance

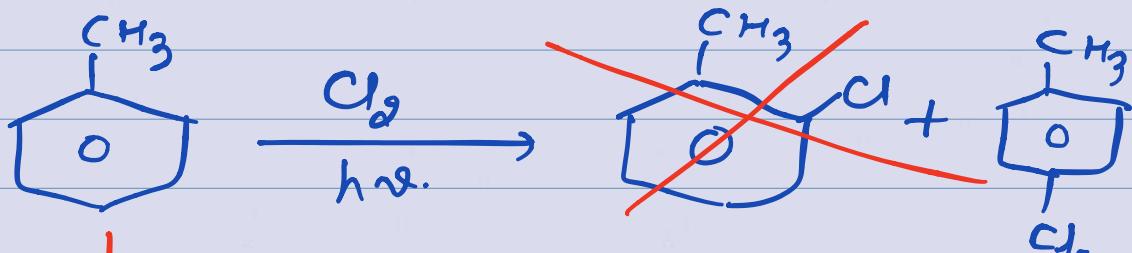
\* TR → Any alkyl group



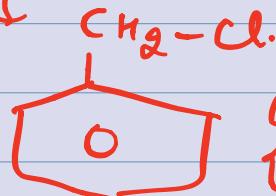


\* It is not  
electrophilic  
subs + on.

\* It is free  
radical addition



$h\nu.$

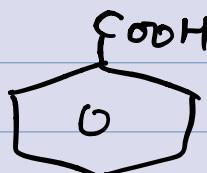
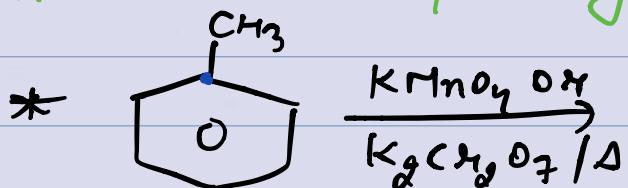


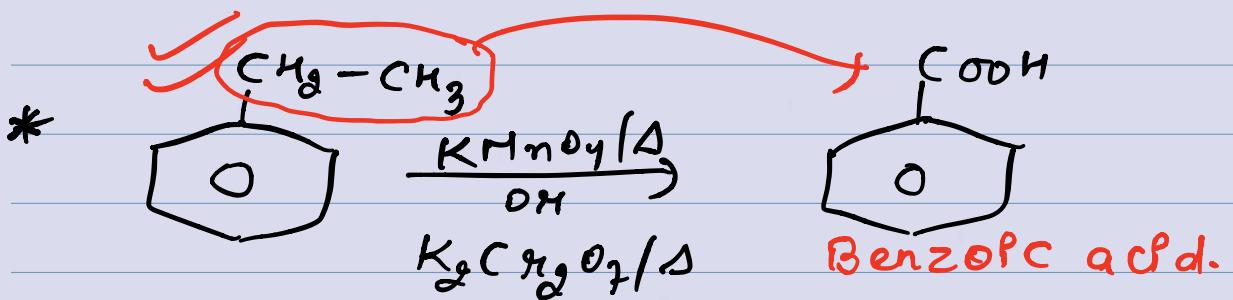
{major}

free radical addition.



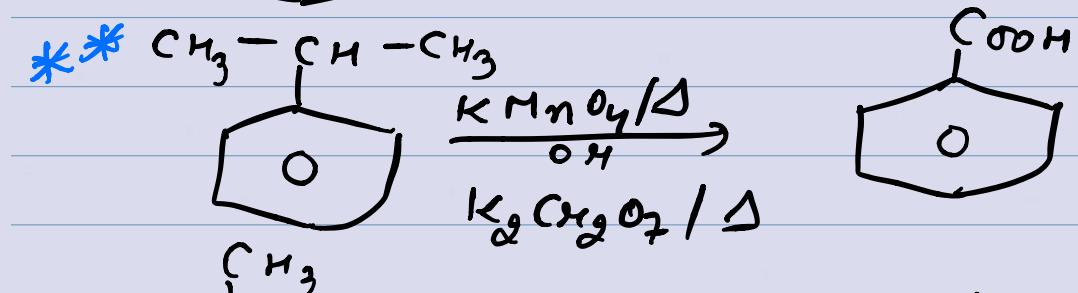
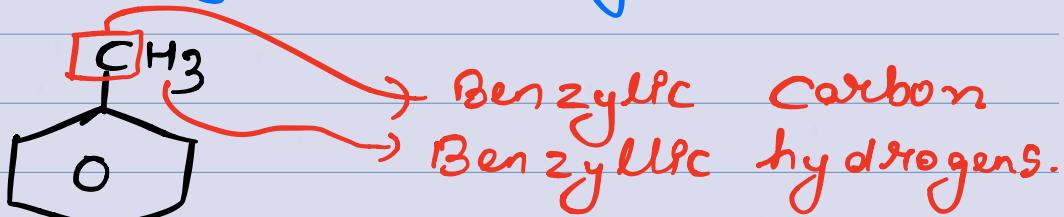
# Oxidation of alkyl benzene  $\text{O}^-$

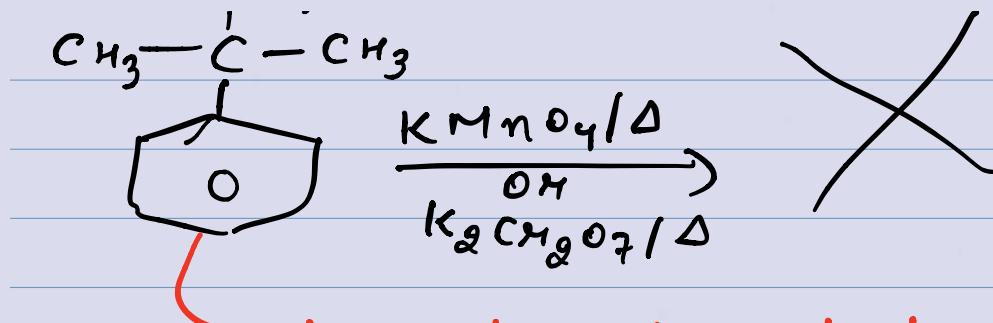




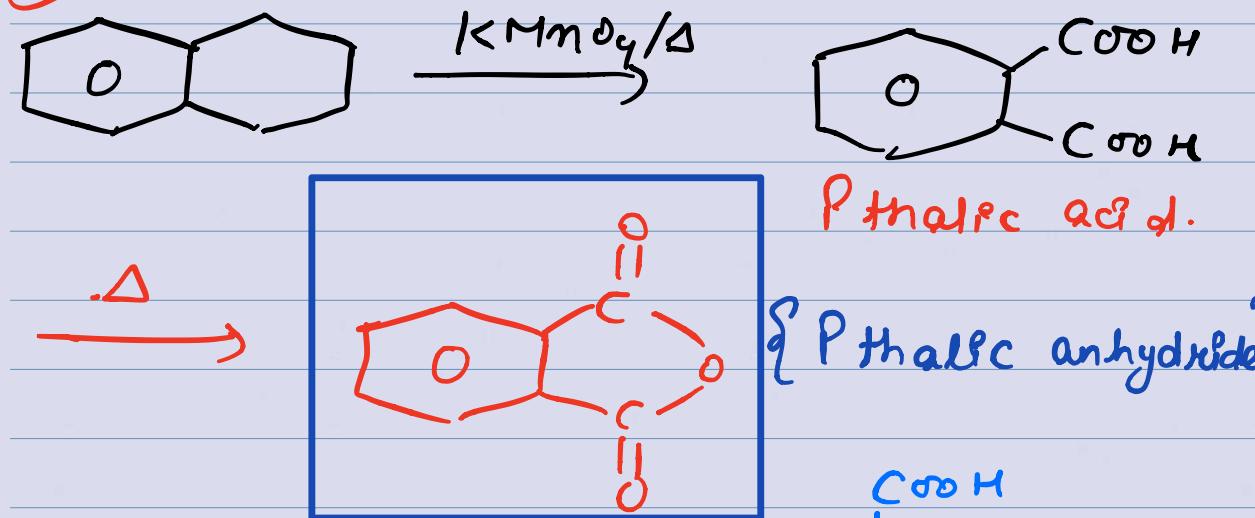
\* No matter how much bigger is the size of alkyl group attached with benzene, those alkyl substituted benzene will be always converted into benzoic acid.

**Note** Alkyl substituted benzene will be converted into benzoic acid, but there must be minimum one benzylic hydrogen atom



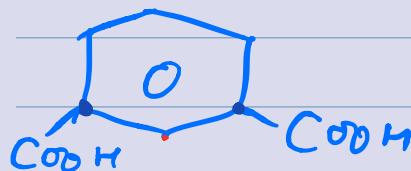


~~Imp.~~  
 no benzyllic hydrogen,  
 no oxidation.

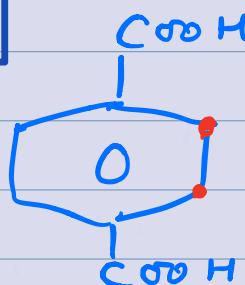


Phthalic acid.

{ Phthalic anhydride }



Iso phthalic acid.



Terphthalic acid.

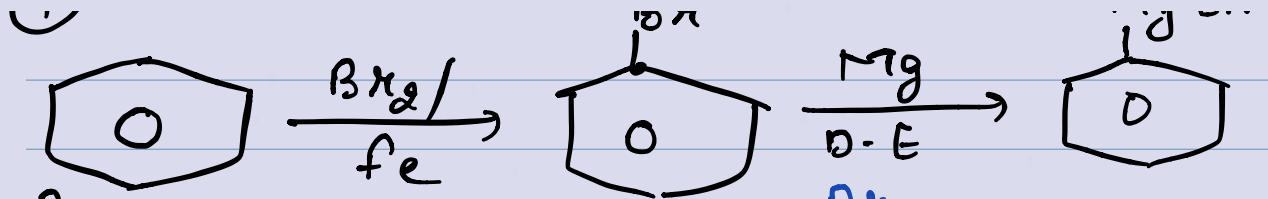
# Benzene acid :-

# Preparation :-

(1)

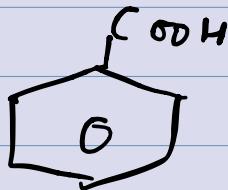
Na

Mar

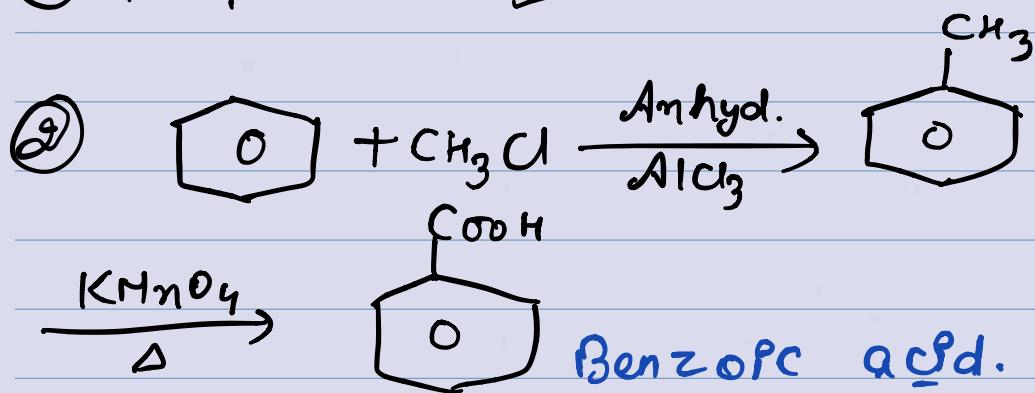


Benzene

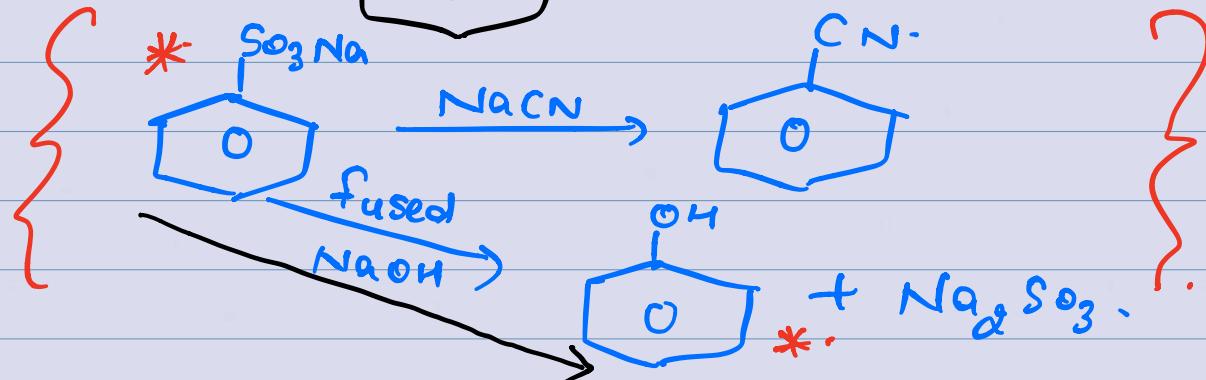
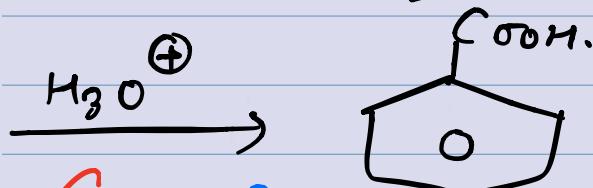
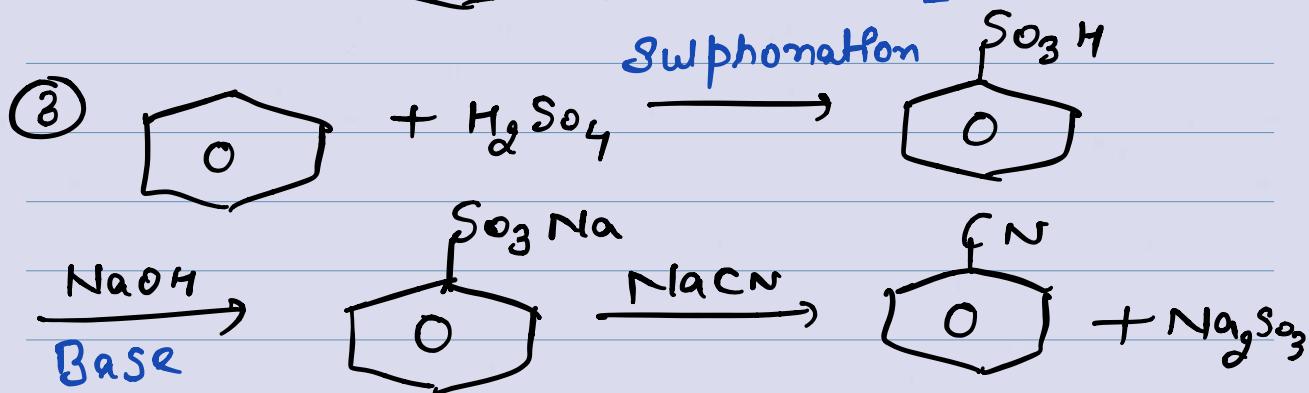
- ①  $\text{CO}_2$   
 ②  $\text{NH}_4\text{Cl}$



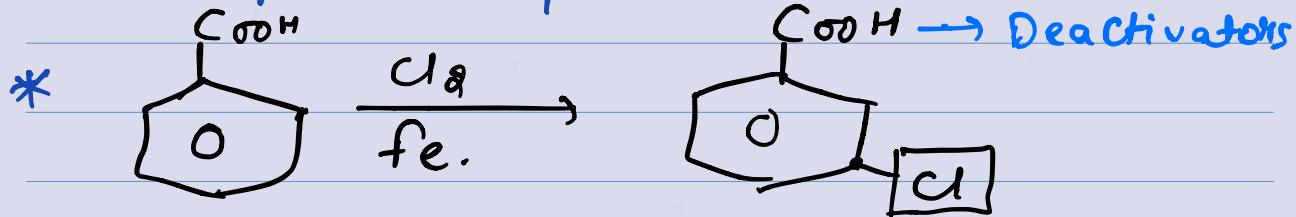
Dry ether.



Benzopic acid.



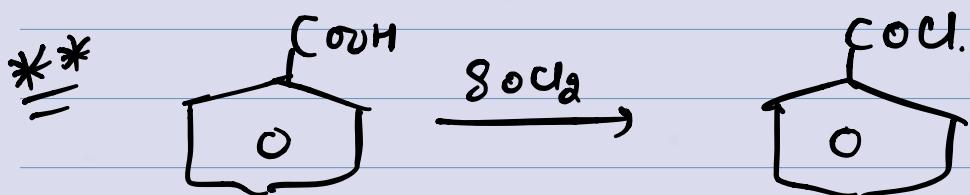
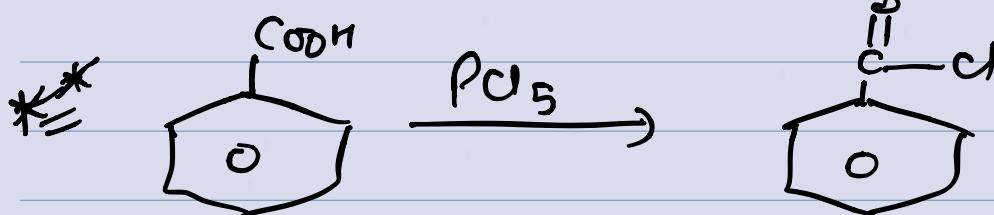
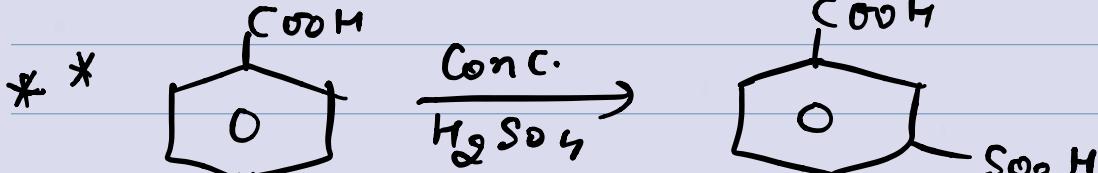
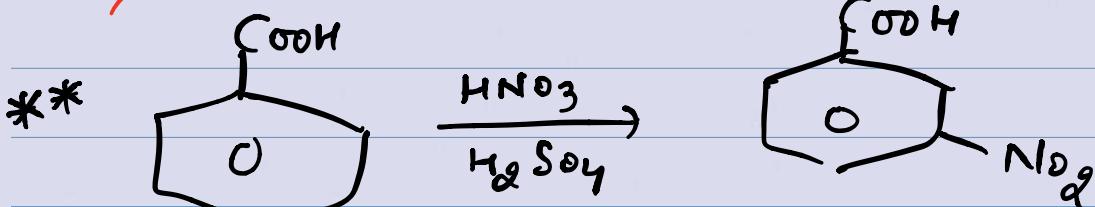
## Properties of benzoic acid :-



$\text{CH}_3-\text{Cl}$   
Anhyd  $\text{AlCl}_3$

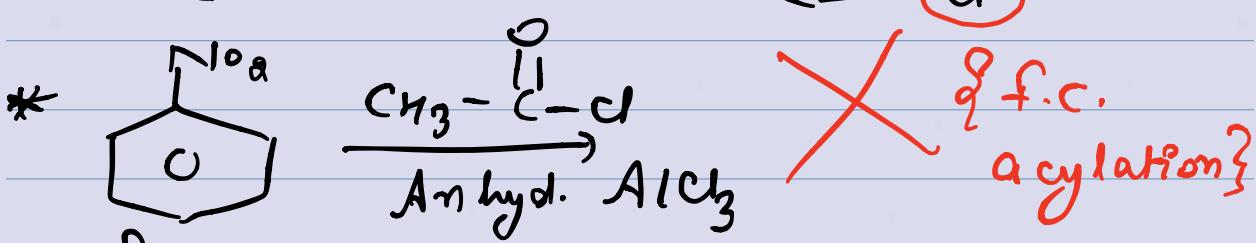
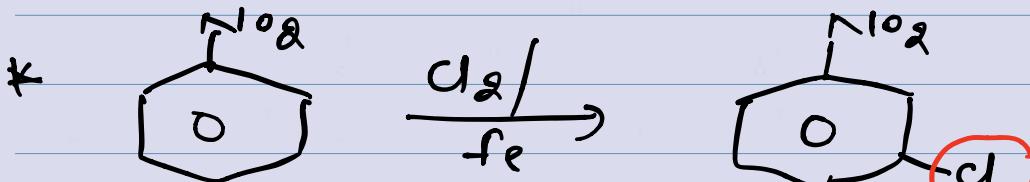
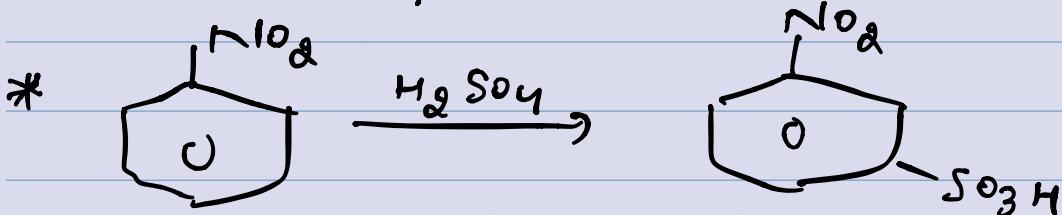
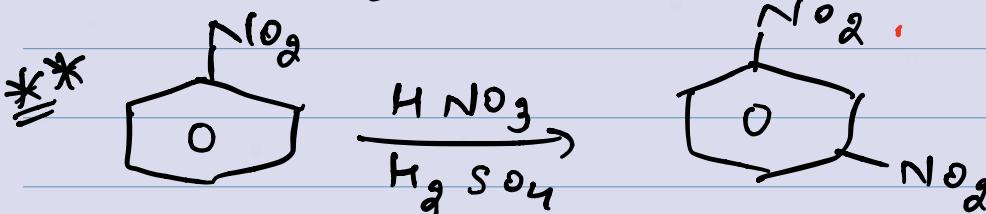
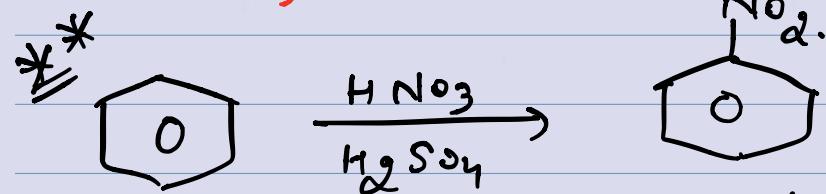


\* f.c. rxns are given by benzene and  $\text{P}+8$  activators - to form Compounds.

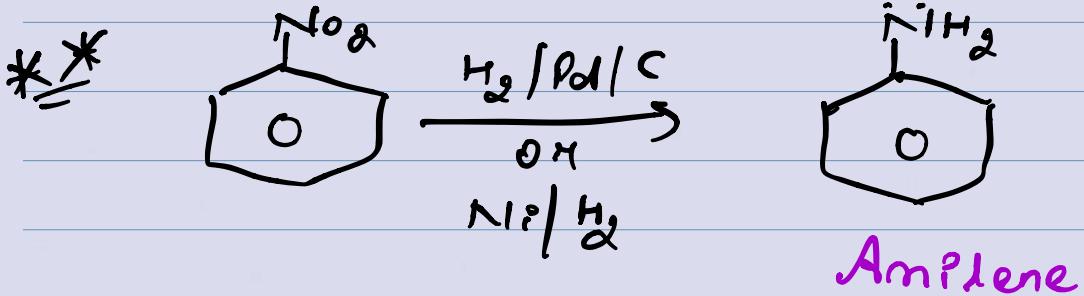


Imp.

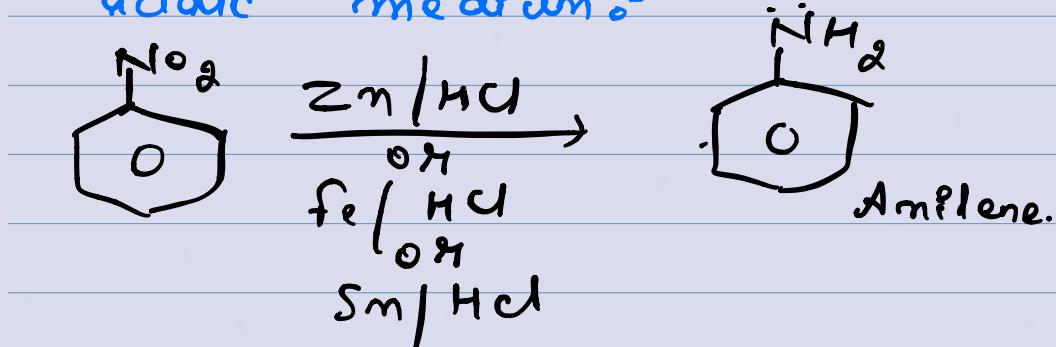
~~#~~ Nitro benzene  $\text{O}^-$



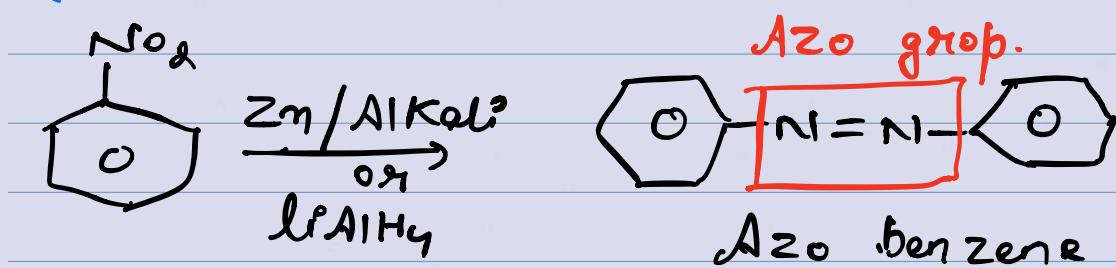
~~#~~ Reduction of nitrobenzene  $\text{O}^-$



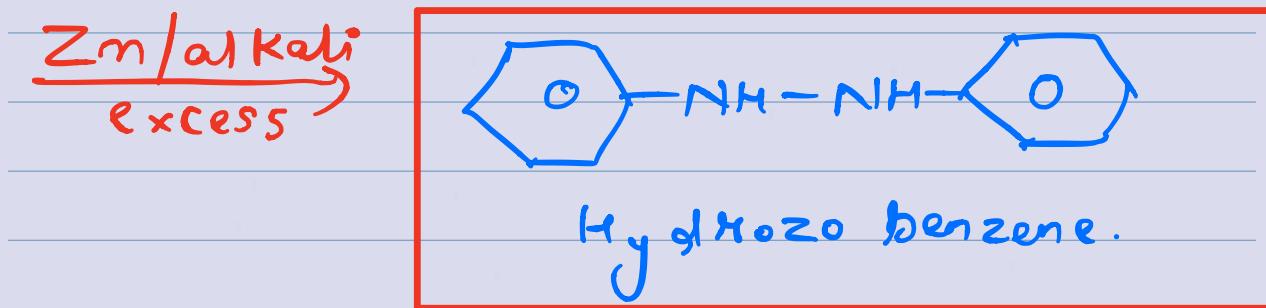
1.) Reduction of m-nitrobenzene in acidic medium :-



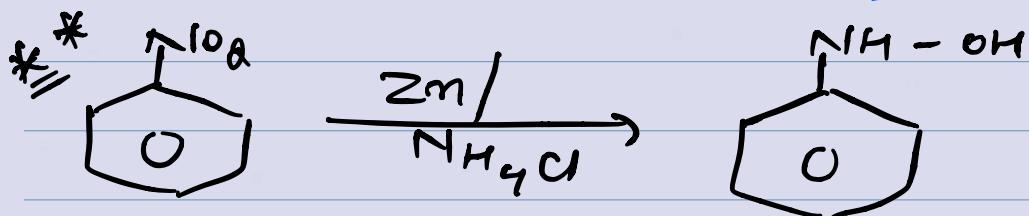
2.) In basic medium :-



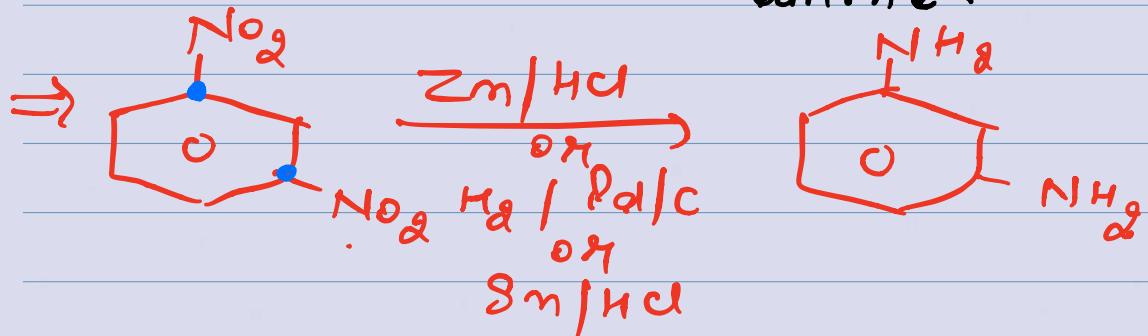
\* If Zn/ alkali is used in excess amount.



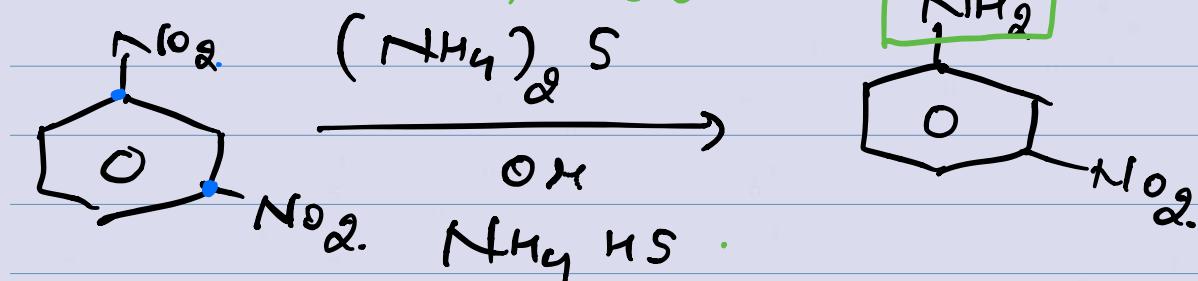
3.) In neutral medium :-



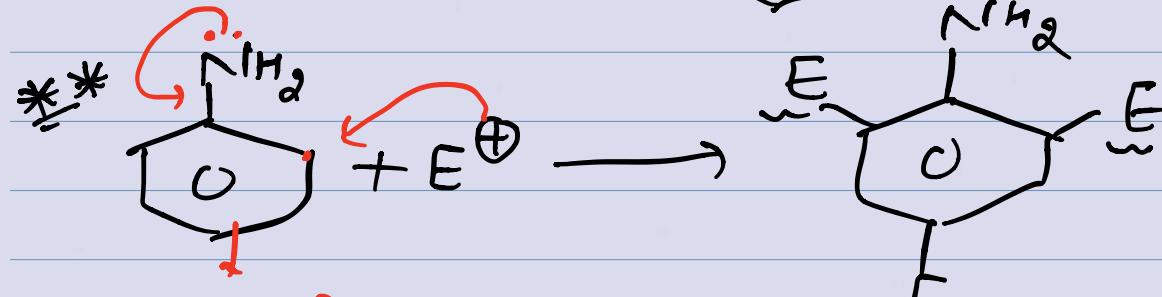
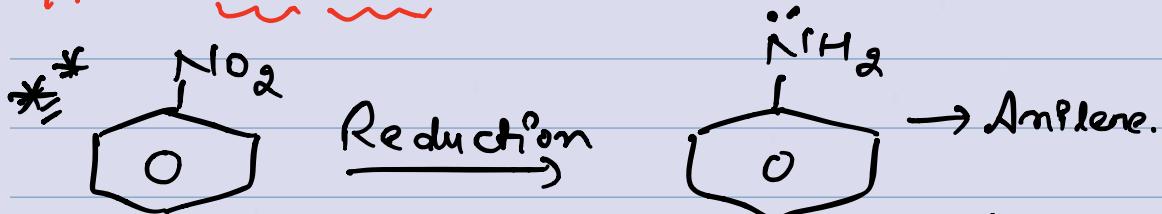
## Phenyl hydroxyl amine.



# Selective reduction of dimethoxybenzene  $\ddot{\sigma}$



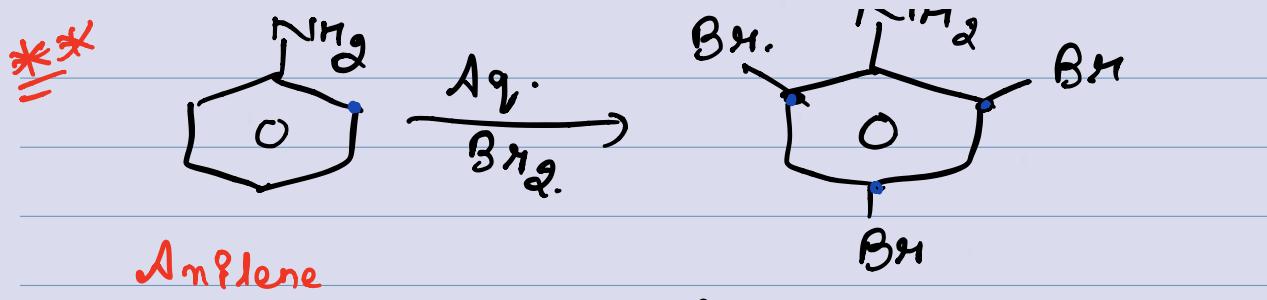
# Amidene  $\ddot{\sigma}$



very strong activator due to presence of 1-p

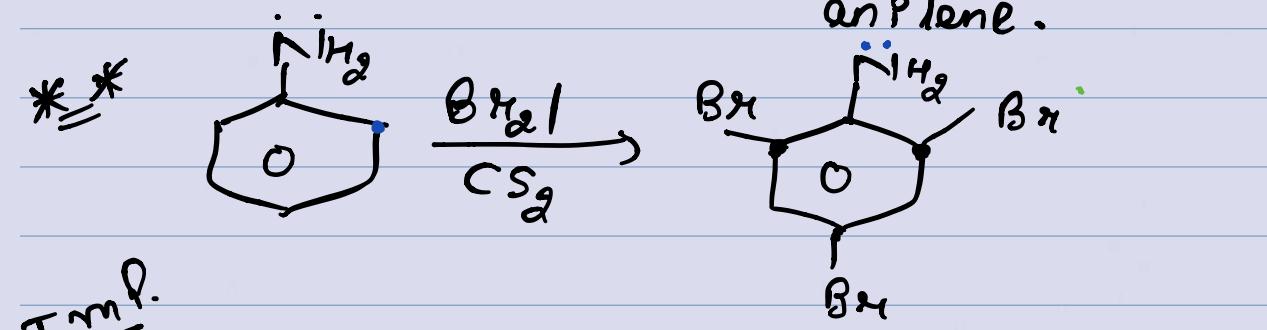
..

z n.



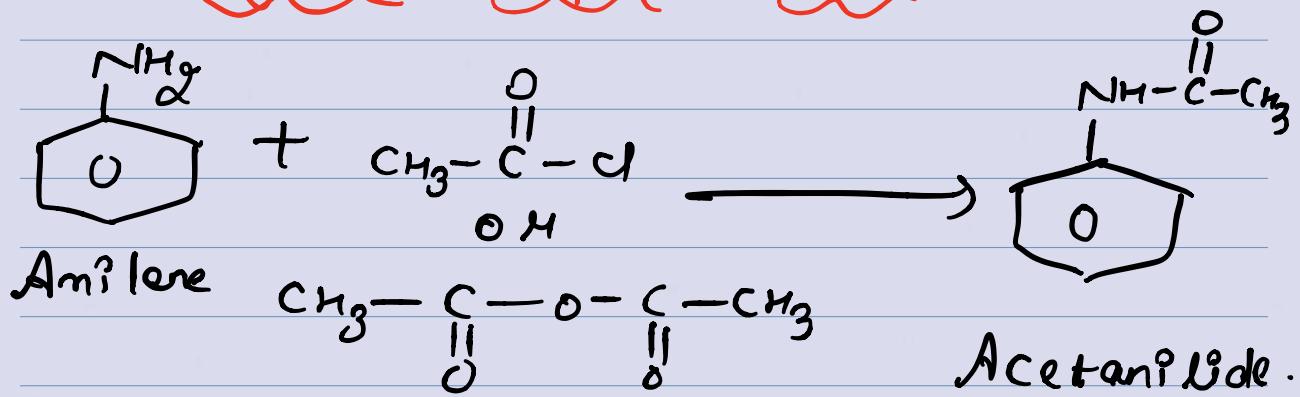
2, 4, 6 tri<sup>o</sup> bromo

anilene.



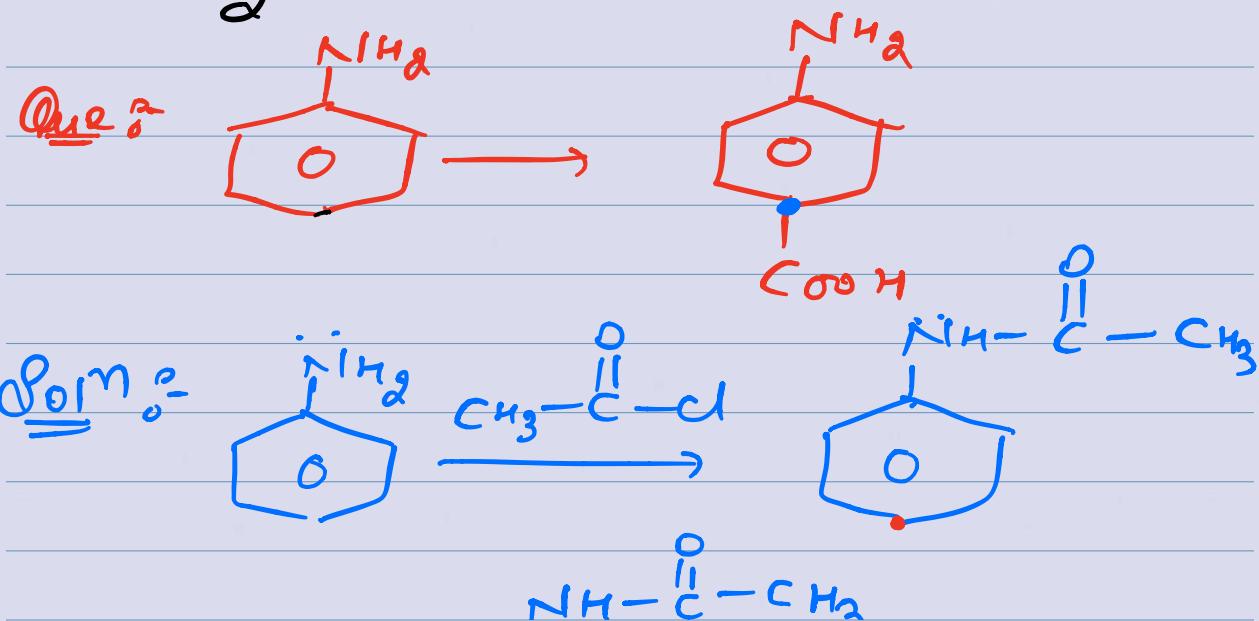
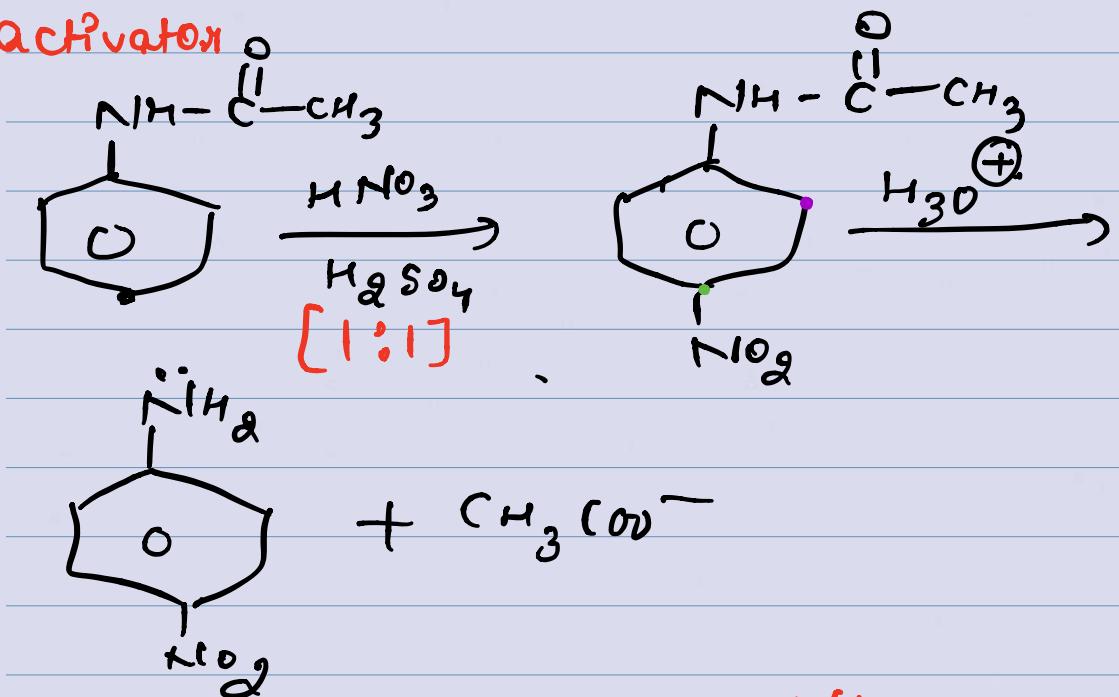
~~\*~~~~\*~~ Anilene is a very strong activator that's why it gives 2, 4, 6 tri<sup>o</sup> substituted electrophilic substitutions

## # Acylation of Anilene

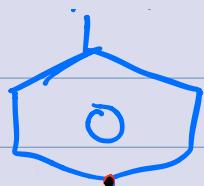


\* Acetanilide is a moderate activator.

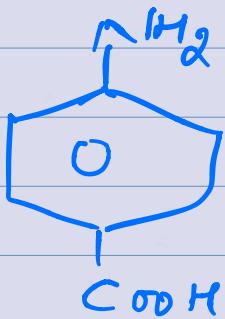
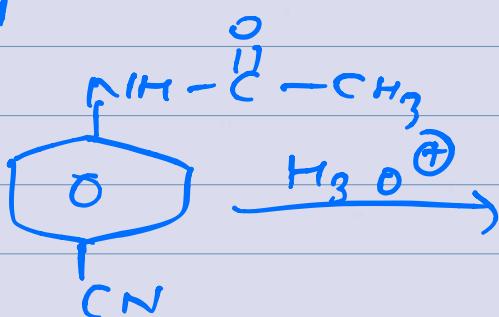
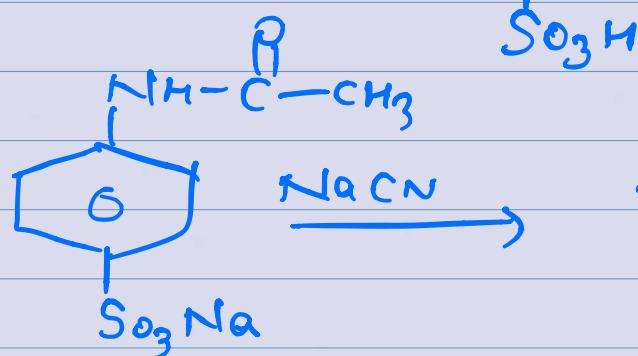
\*\* To attack an electrophile at a particular position in anilene, it will be converted into acetanilide which is a moderate activator.



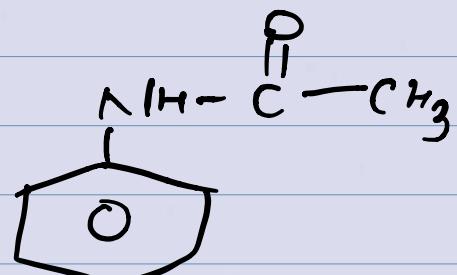
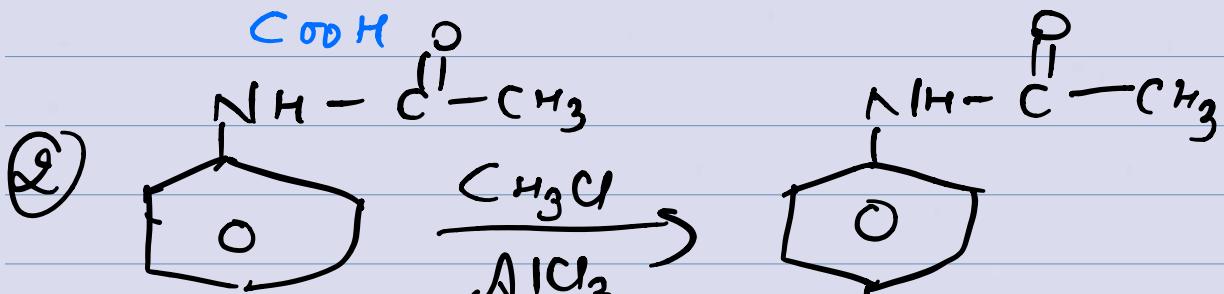
Sulphonation



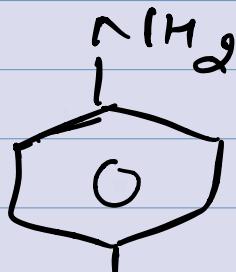
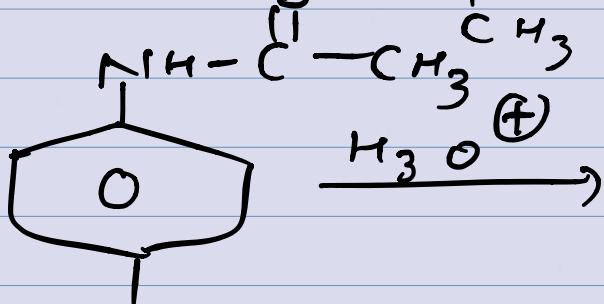
NaOH



COOH

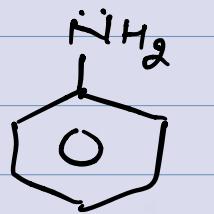


$\xrightarrow[\Delta]{KMnO_4}$

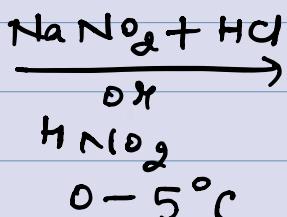


CODH

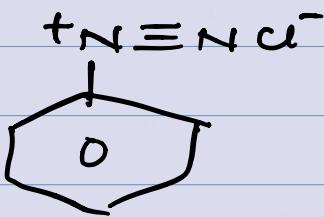
## # Diazotisation of Aniline $\text{O}^-$



Aniline

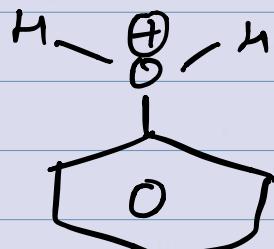
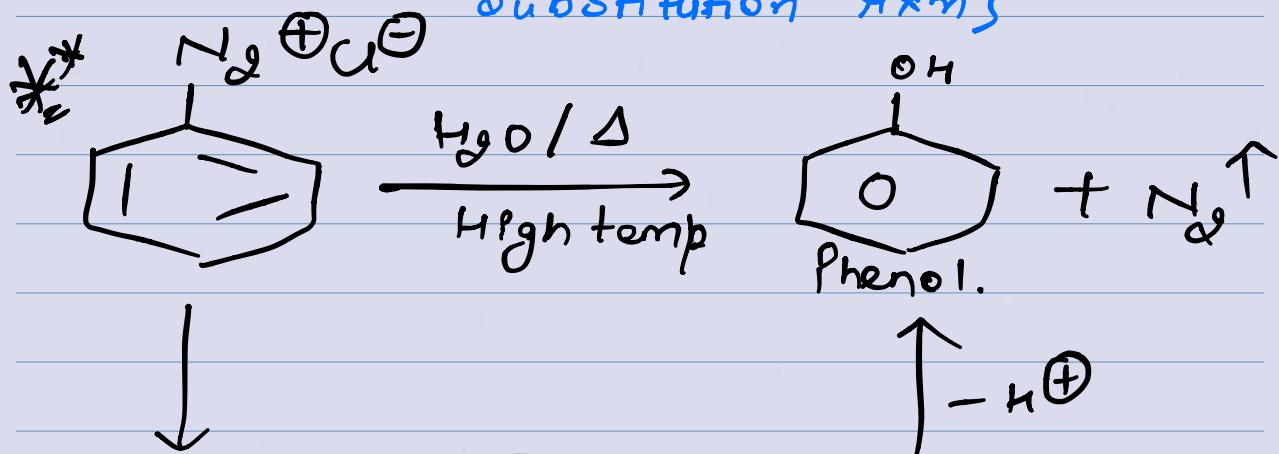


$0 - 5^\circ\text{C}$

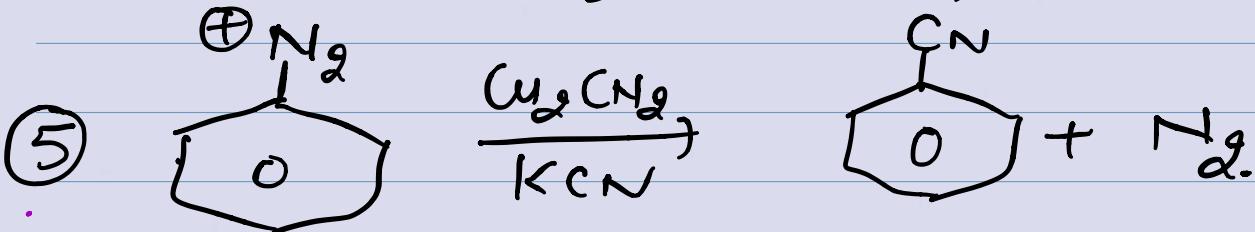
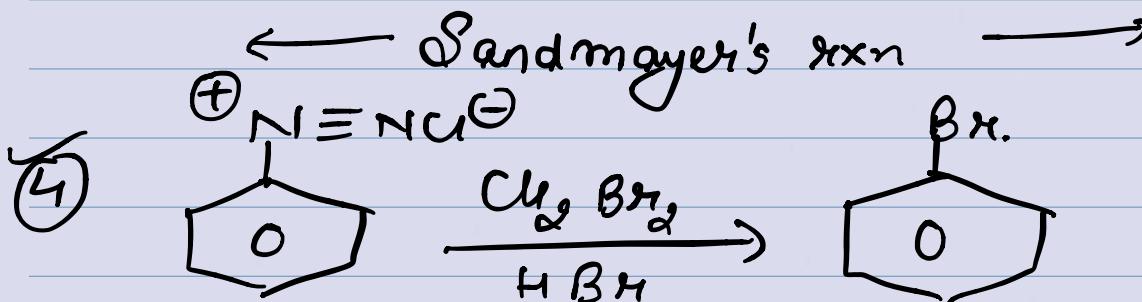
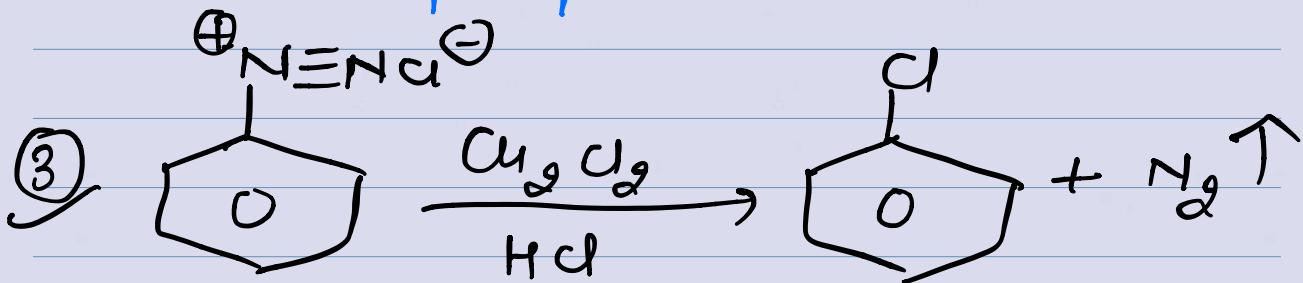
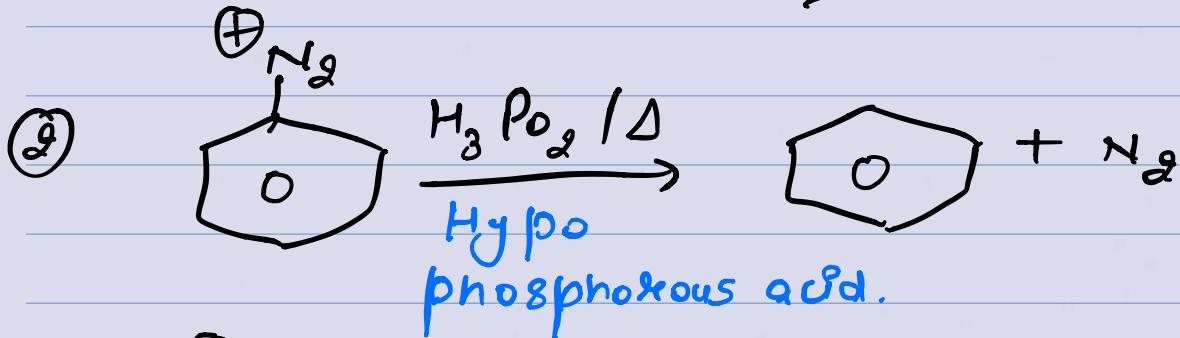
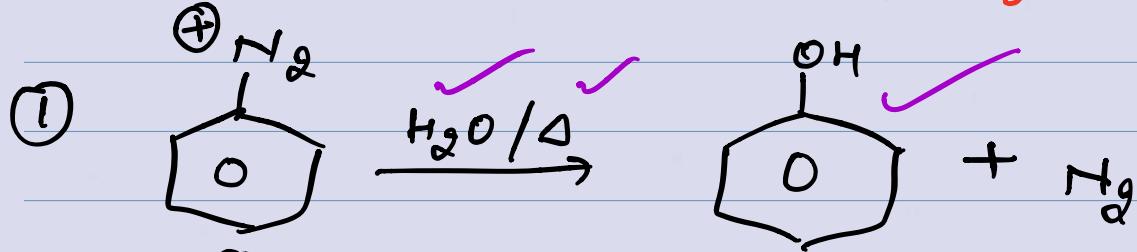


Benzene diazonium  
chloride.

$\Rightarrow$   $\text{ArSN}' \}$  Aromatic unimolecular  
substitution  $\text{ArX}$

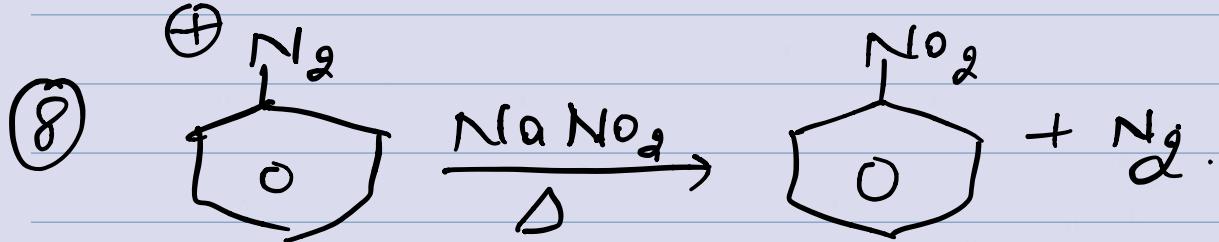
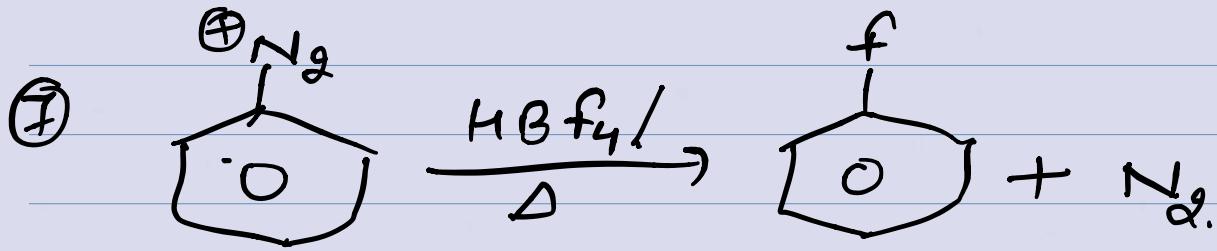
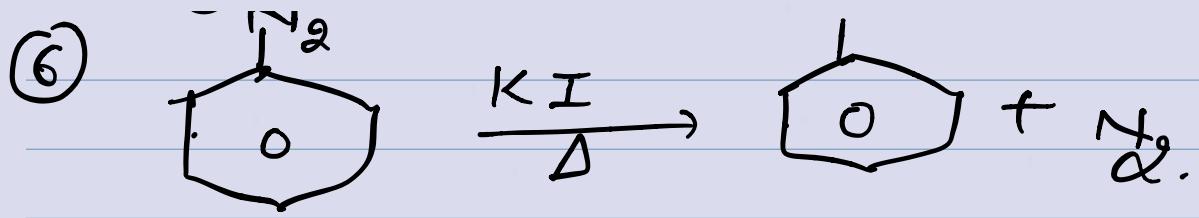


## # Some Important rxns of benzene diazonium salt

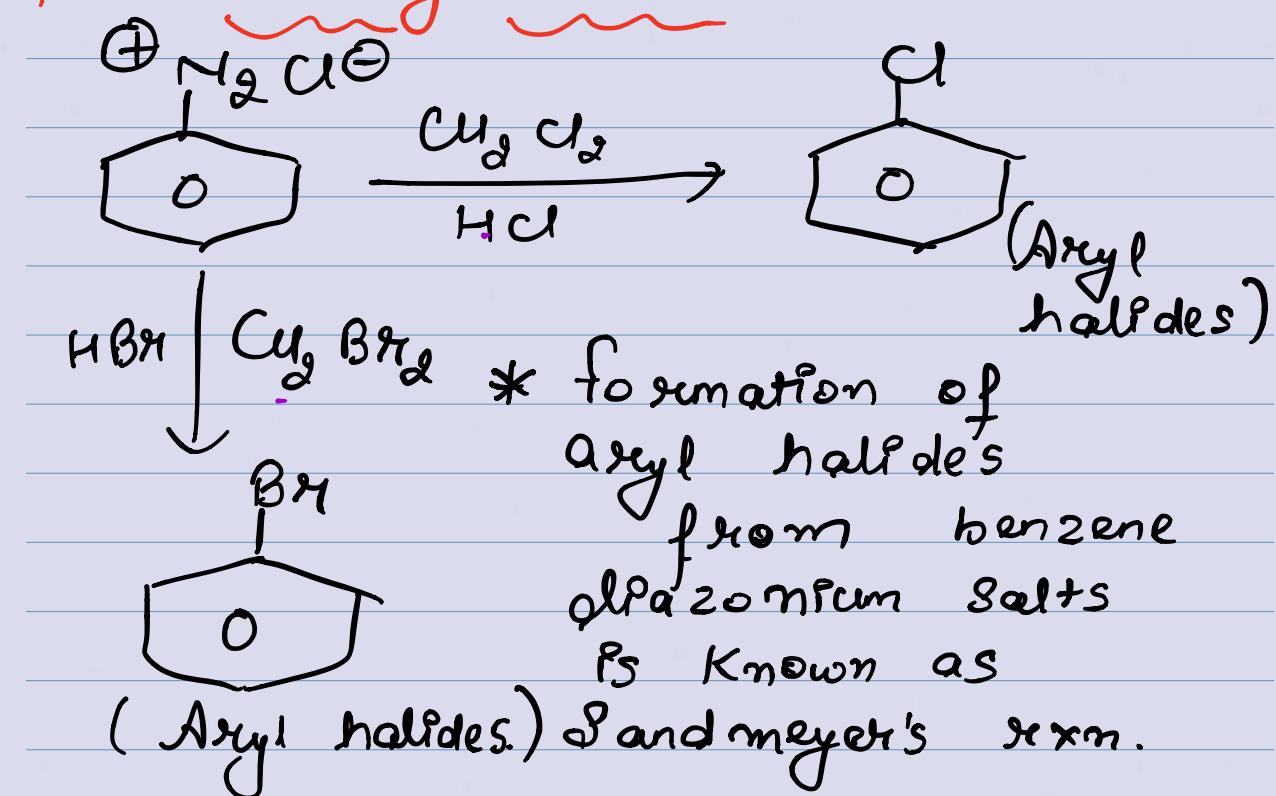


$\oplus_{-1}$

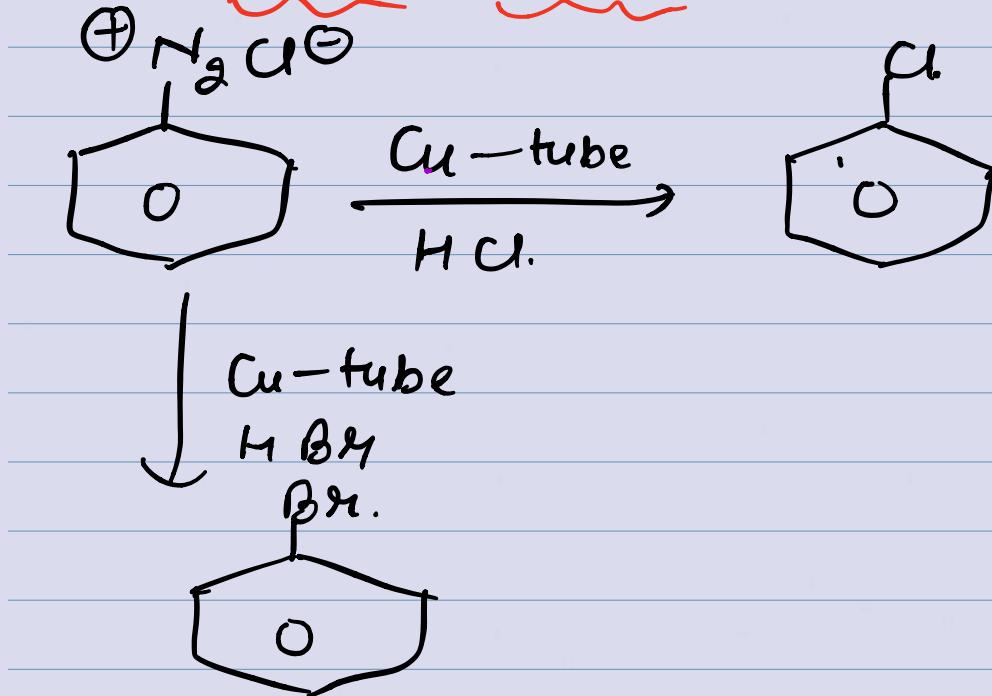
I



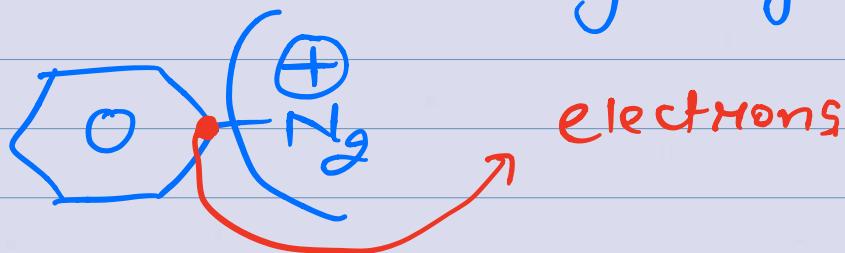
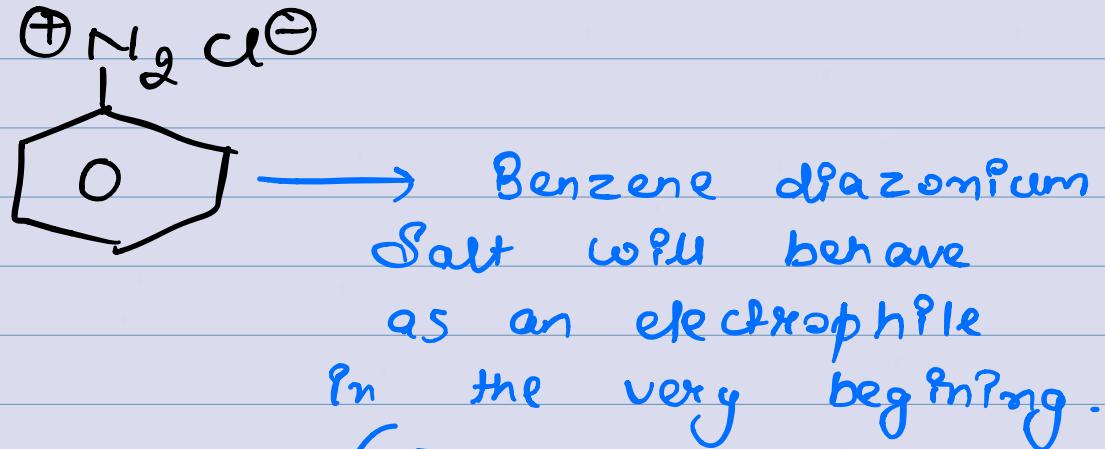
# Sandmeyer's Rxn :-



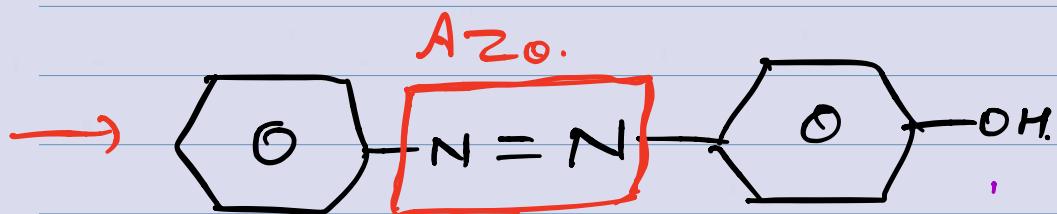
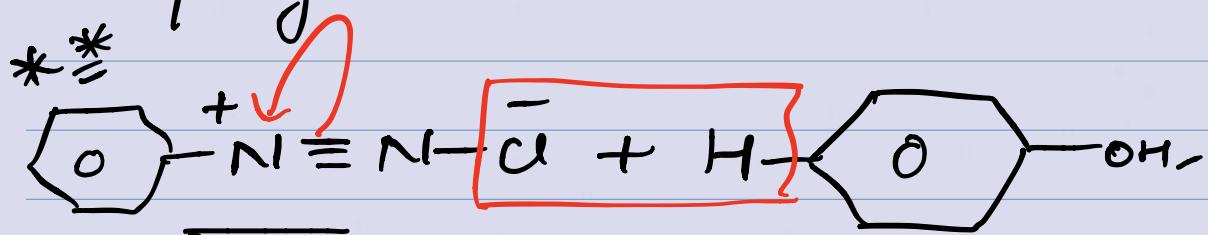
# Grattermann Rxn  $\delta^-$



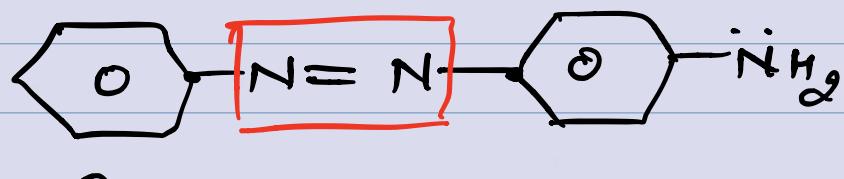
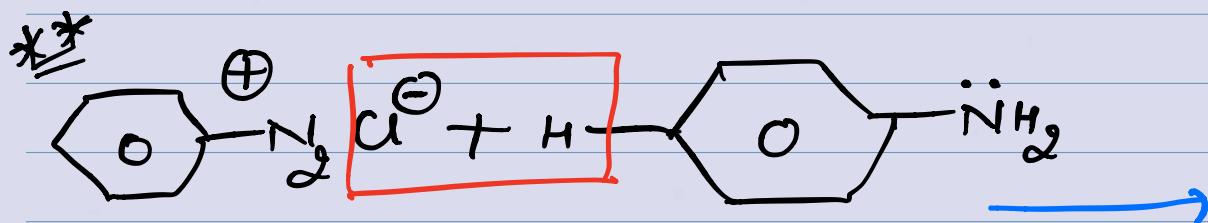
# Coupling Rxn of benzene diazonium salt  $\delta^-$



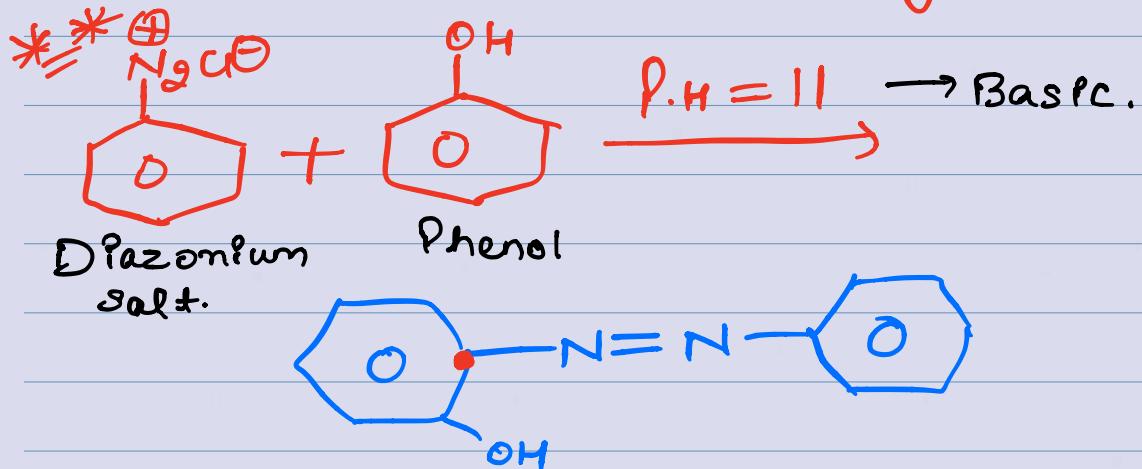
\* when benzene diazonium chloride reacts with strong activator compounds like phenol, aniline etc. then derivatives of azo benzene are formed and these are coloured dyes & rxn is coupling rxn.



Para hydroxy azo benzene.  
 { orange coloured dye }

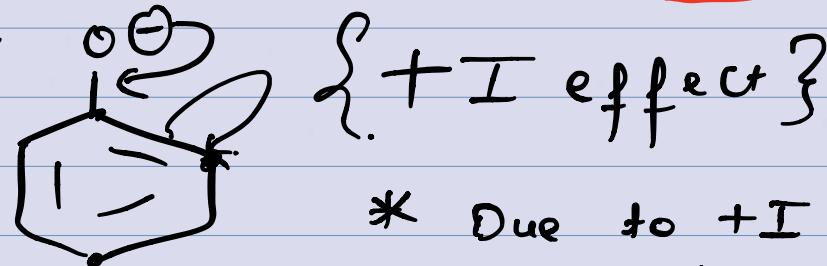
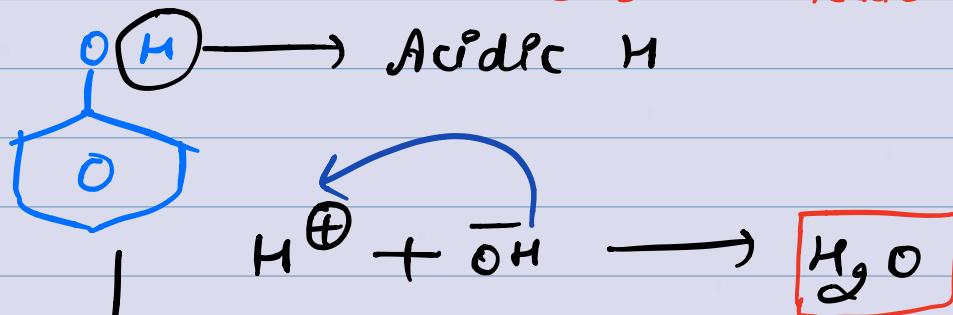


Para amino azo benzene.  
(Yellow Coloured dye)



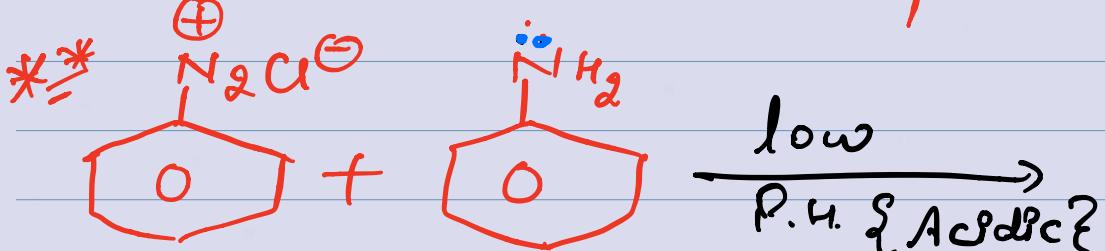
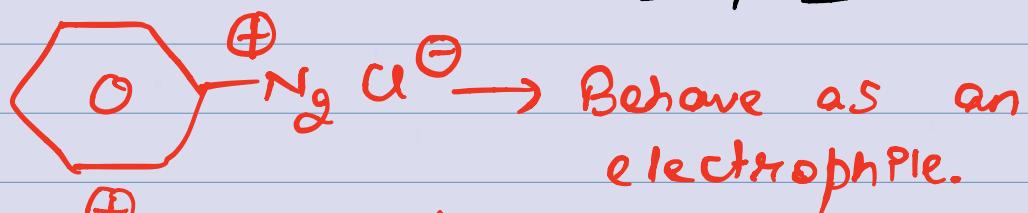
{ Ortho hydroxy azo benzene }

$P.H = 11 \rightarrow \text{Basic medium.}$



\* Due to +I effect

Phenoxyde ion: of phenoxide  
on e<sup>-</sup> density  
will be very high at  
ortho position.

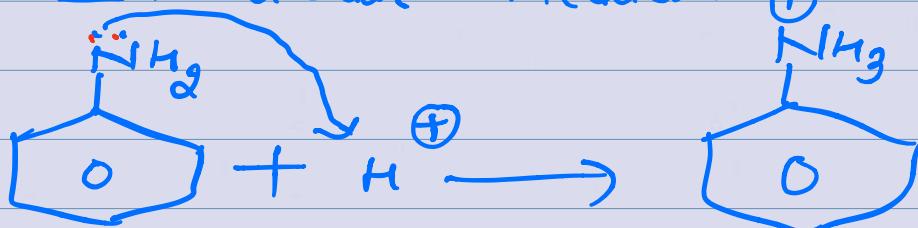


Diazonium Salt

Aniline.

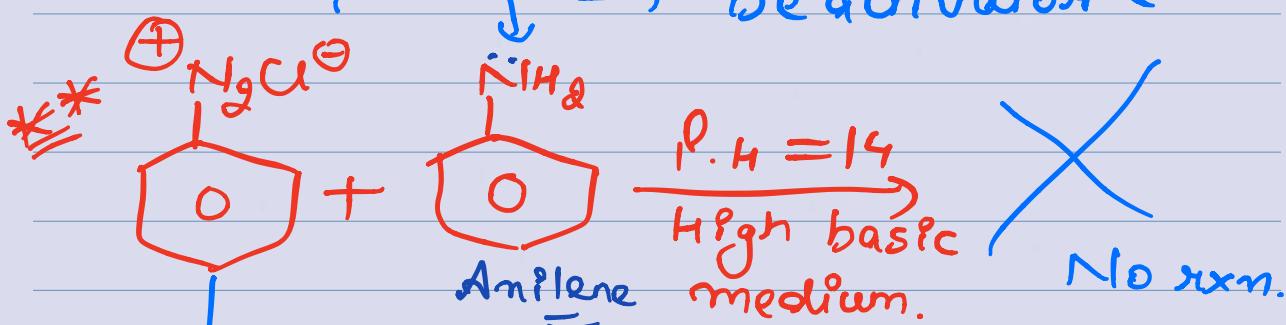
~~No rxn.~~

\* In acidic medium.



{ Anilinium Pm. }

Deactivator ←

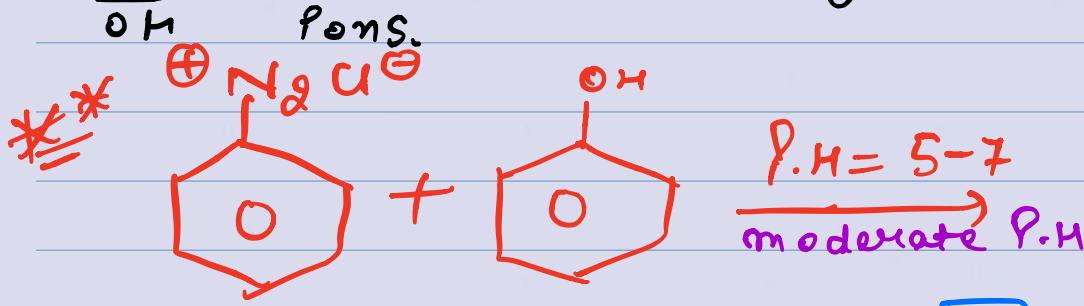


~~No rxn.~~

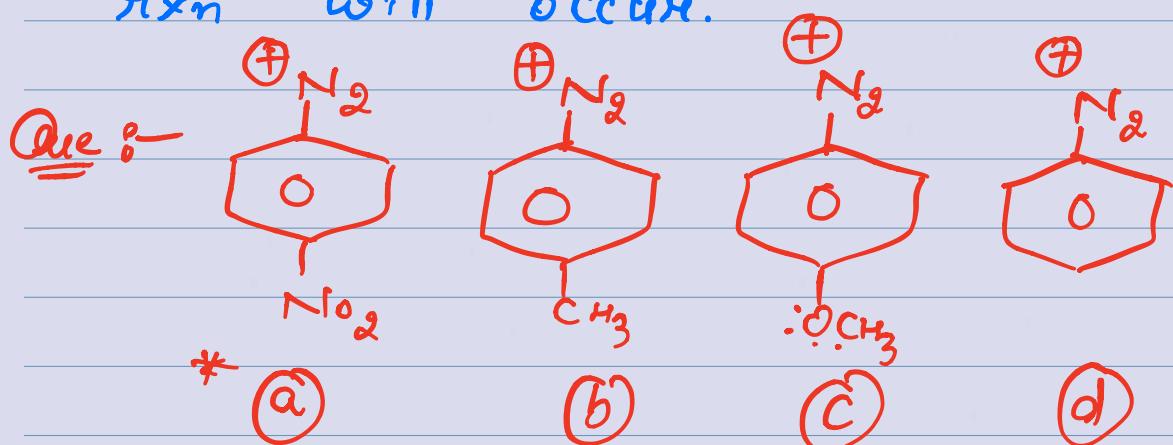
Basic  $\rightarrow \text{OH}^-$  (Plenty)



\* As B.D.C is an electrophile so in very high basic medium instead of reacting with anilene it will start reacting with

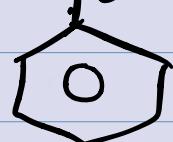
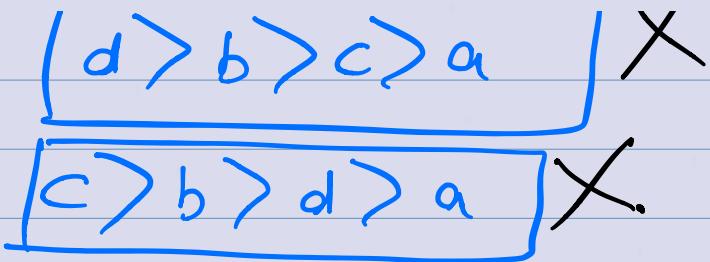


\* At moderate P.H the above rxn will occur.



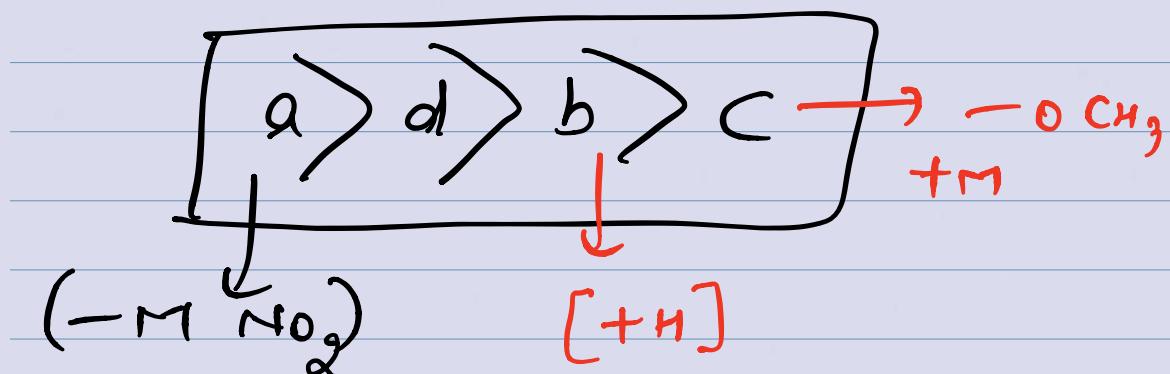
Compare the rate of coupling rxn with phenol.

80%<sup>o</sup>



→ It behaves as an electrophile.

\* Electron withdrawing group increases the electrophilicity of nitrogen hence rate of coupling rxn increases.

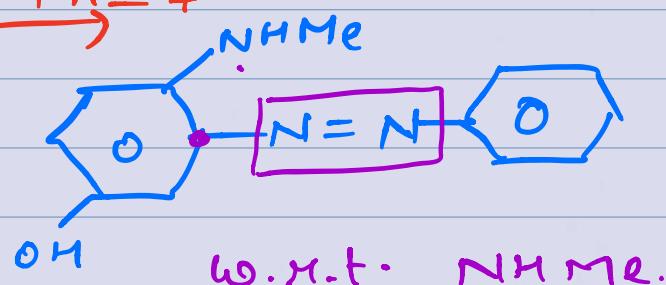
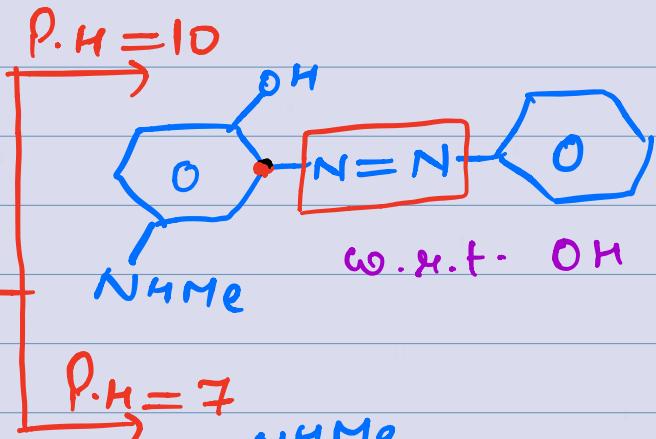
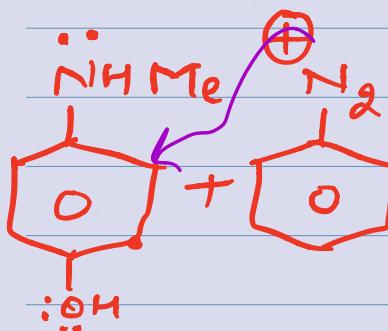


Anisole.

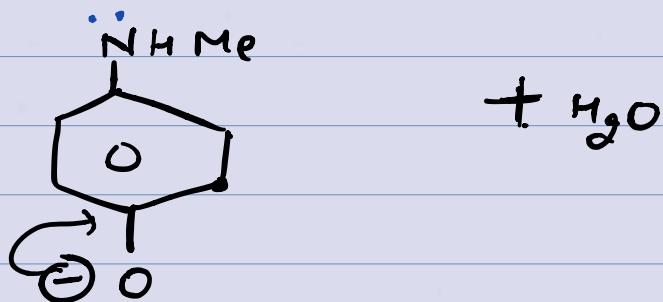
..

\* Anisole do not give coupling rxn with benzene diazonium salt because it is a moderate activator.

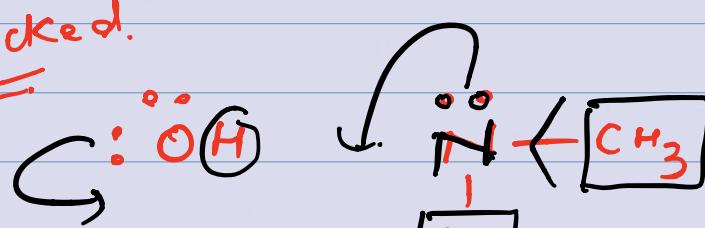
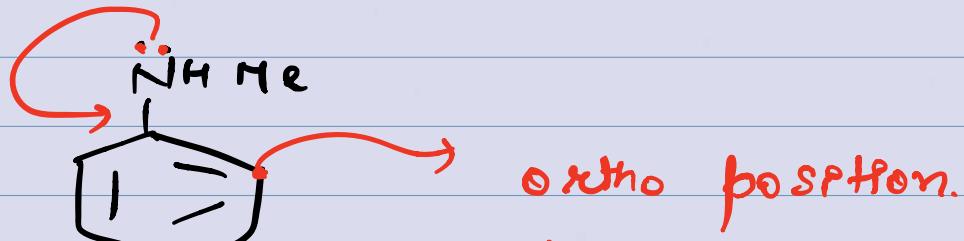
\*\*\*



P.H = 10 → Basic medium

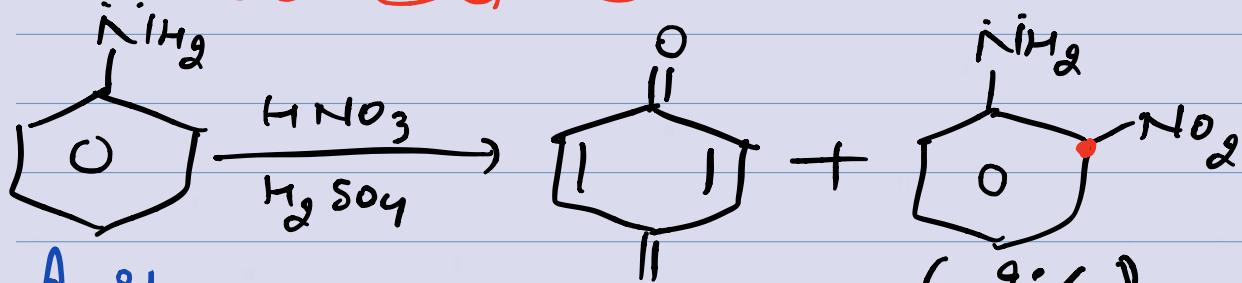


P.H = 7 → neutral.



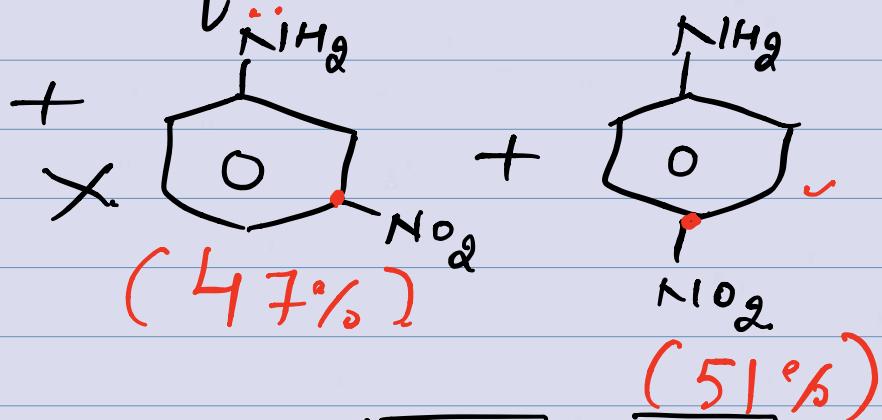
15

## # Nitration of Aniline %

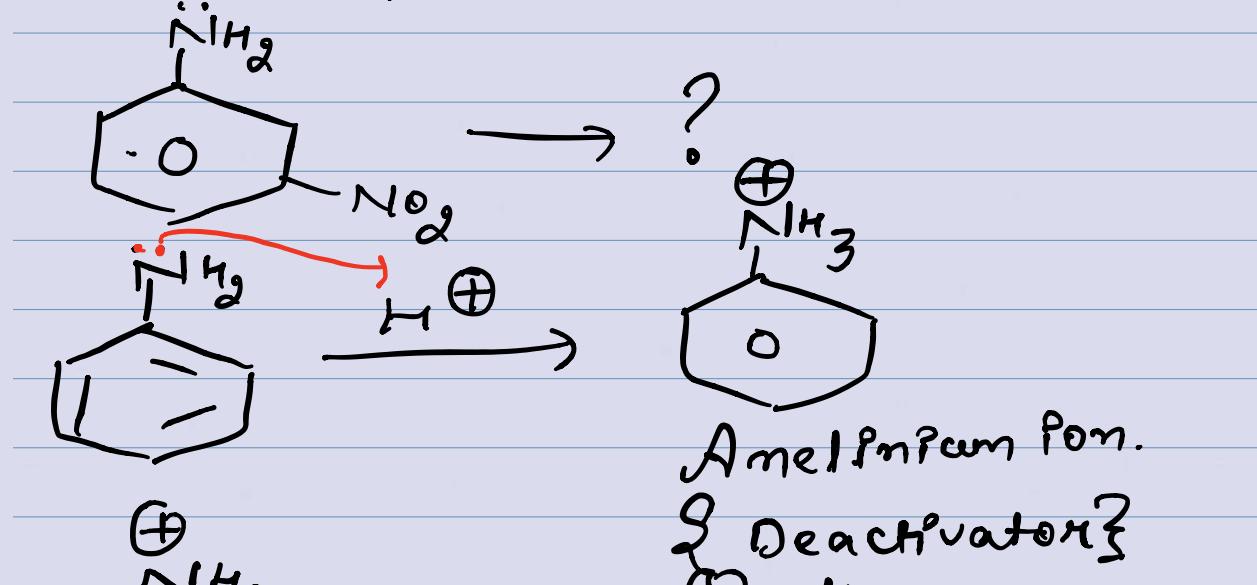


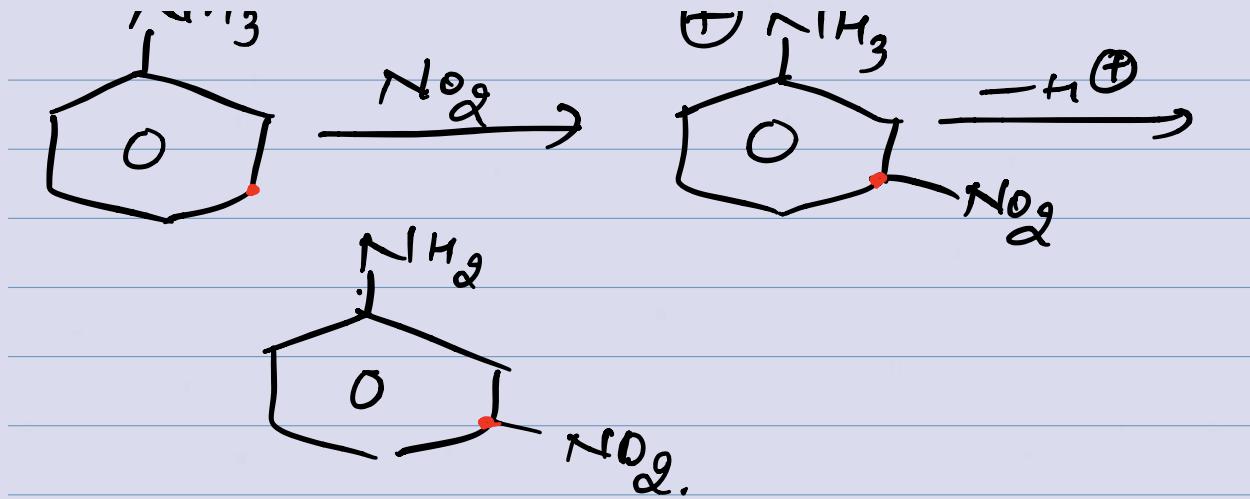
\* Para benzo

quinone.

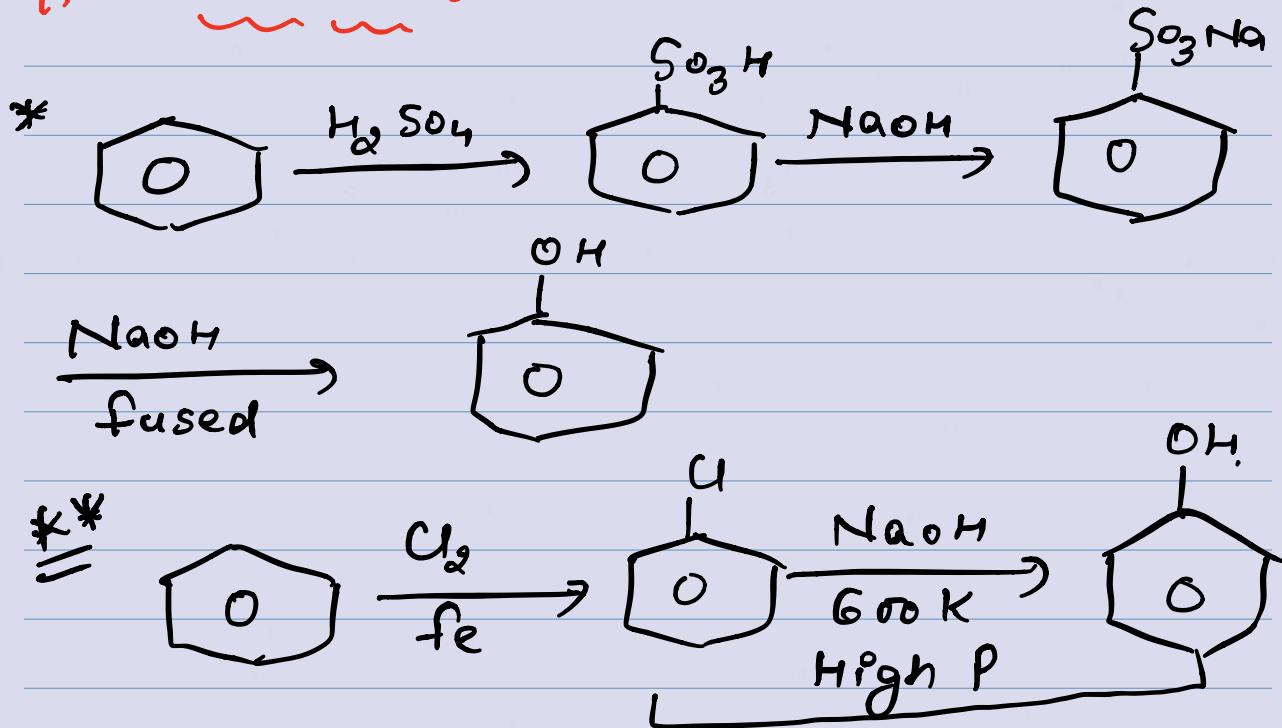


\* Major product → Ortho & Para

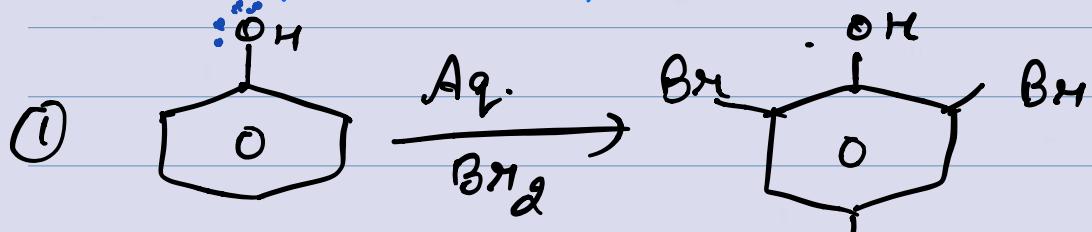


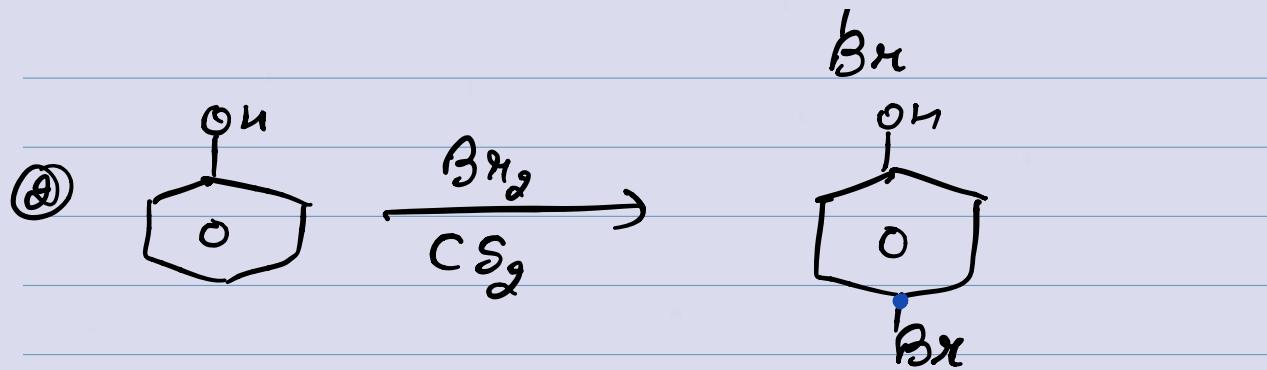


## # Phenol $\text{O}^-$



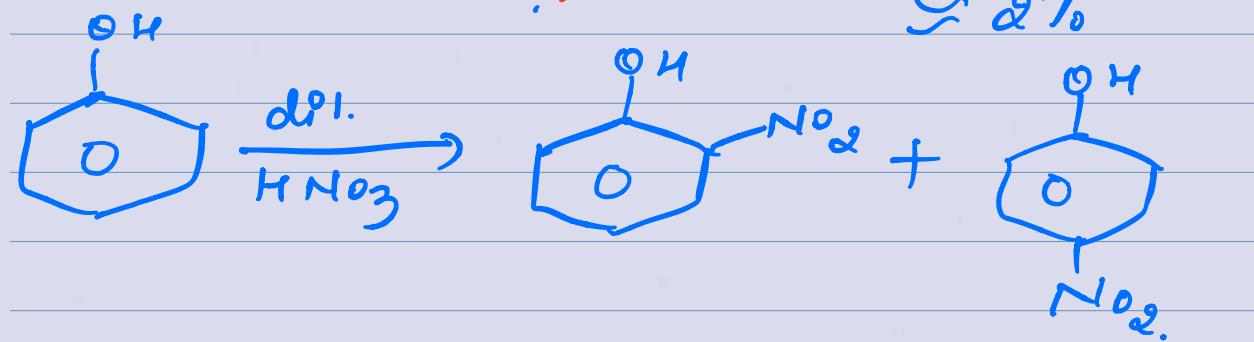
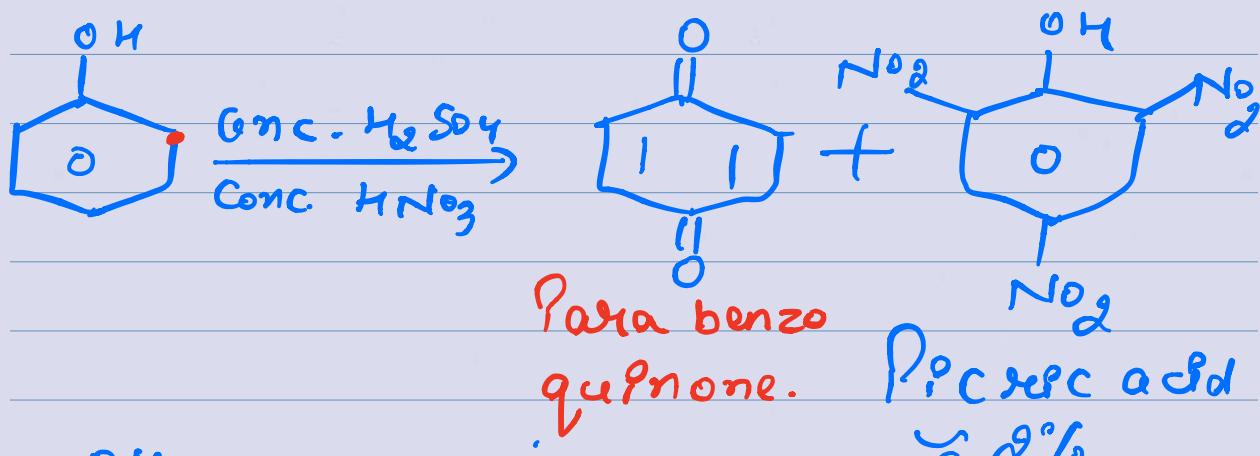
## $\Rightarrow$ Properties of phenol $\text{O}^-$



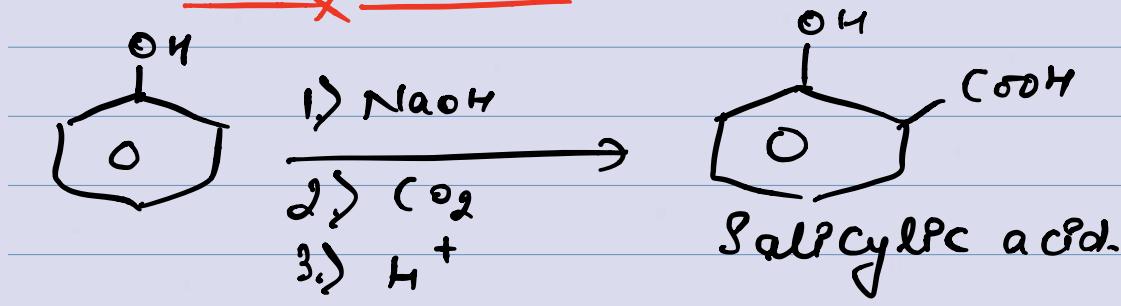


$\Rightarrow$  Nitration of phenol  $\sigma^-$

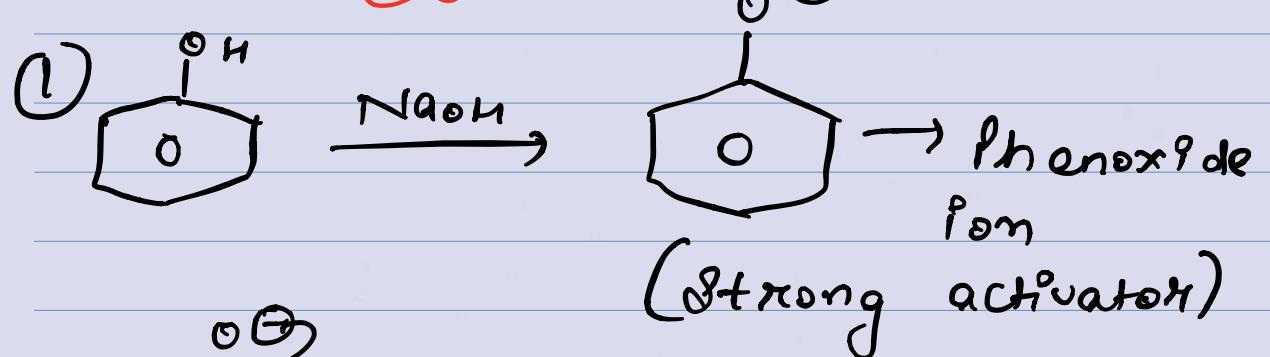
\* As phenol is a strong activator hence its direct nitration is not done.



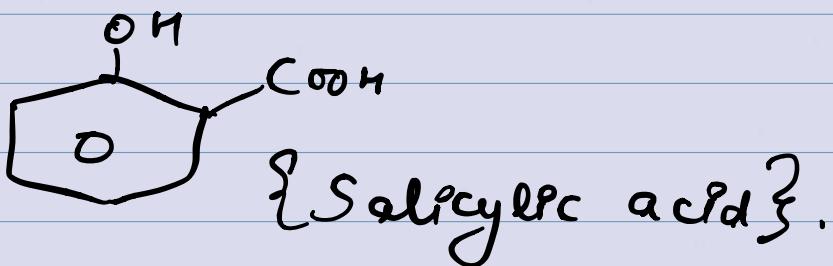
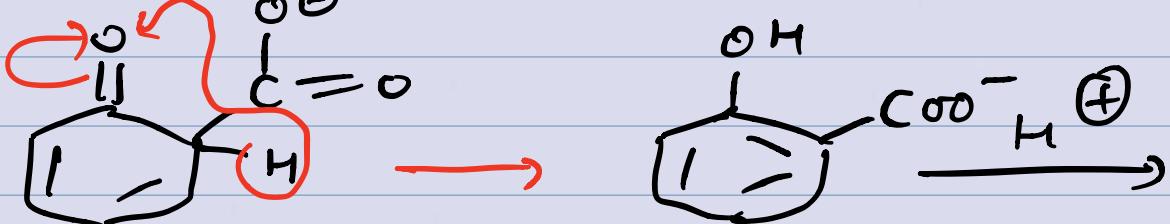
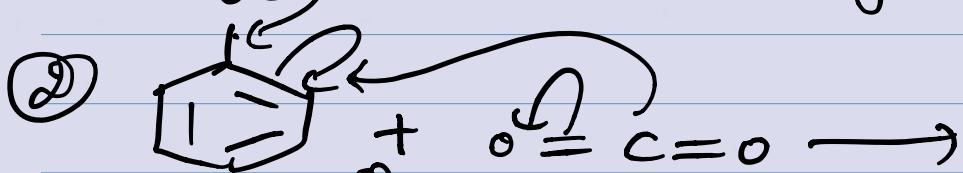
## # Kolbe's Rxn ⚡

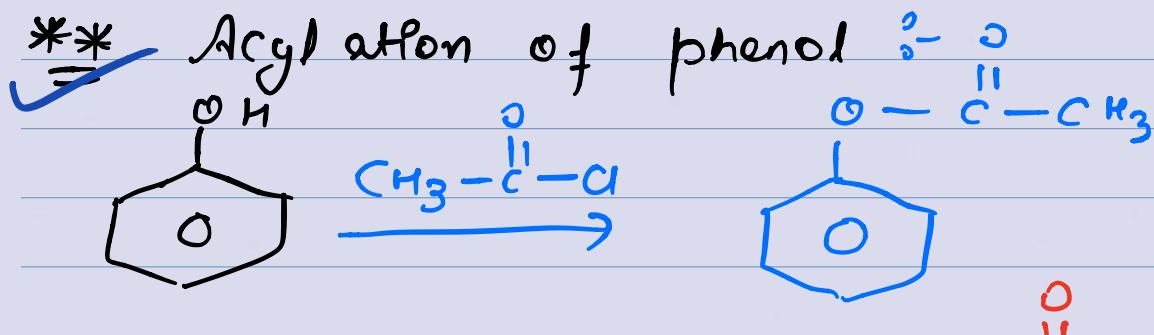
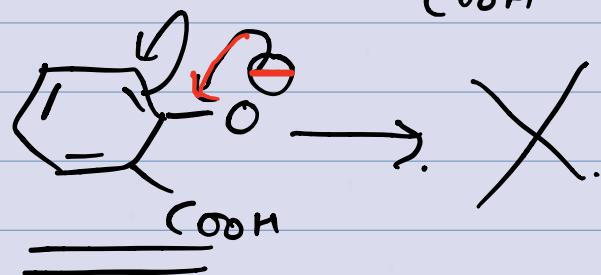
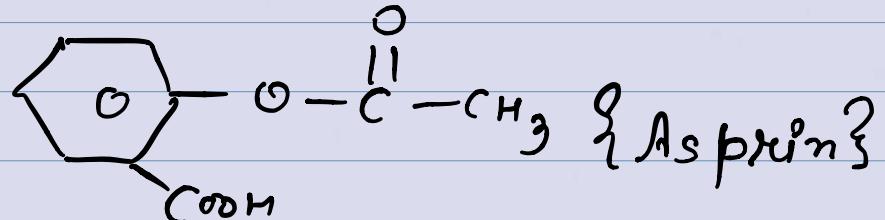
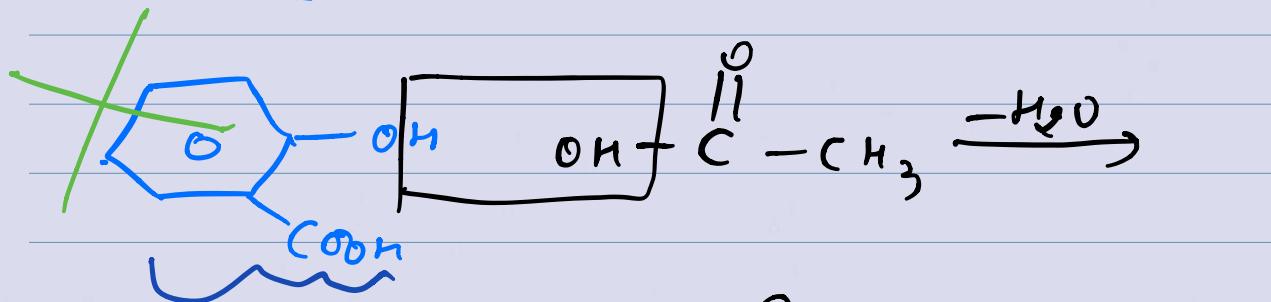
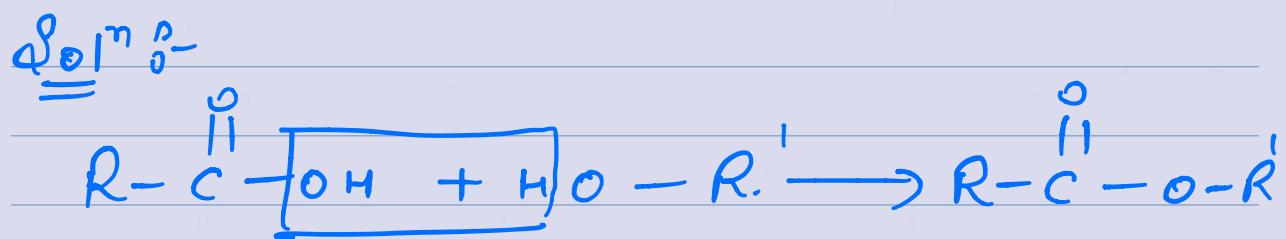
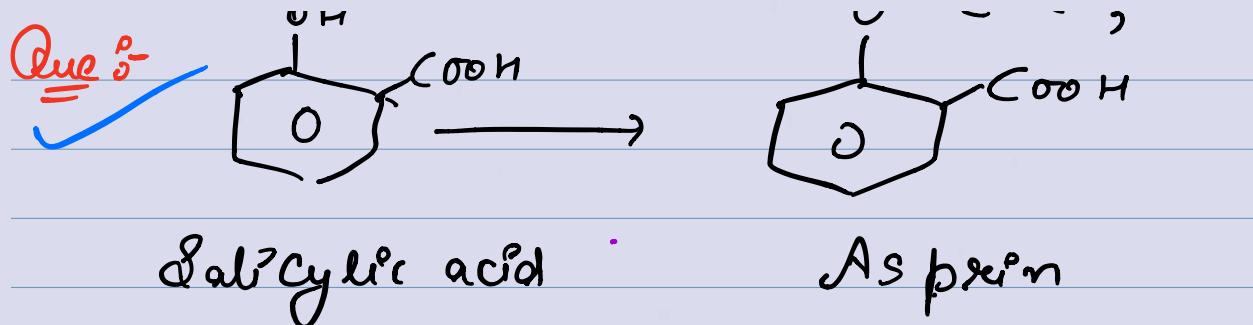


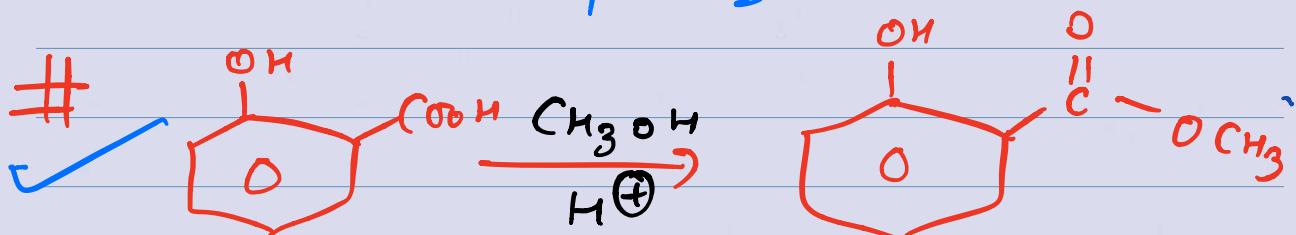
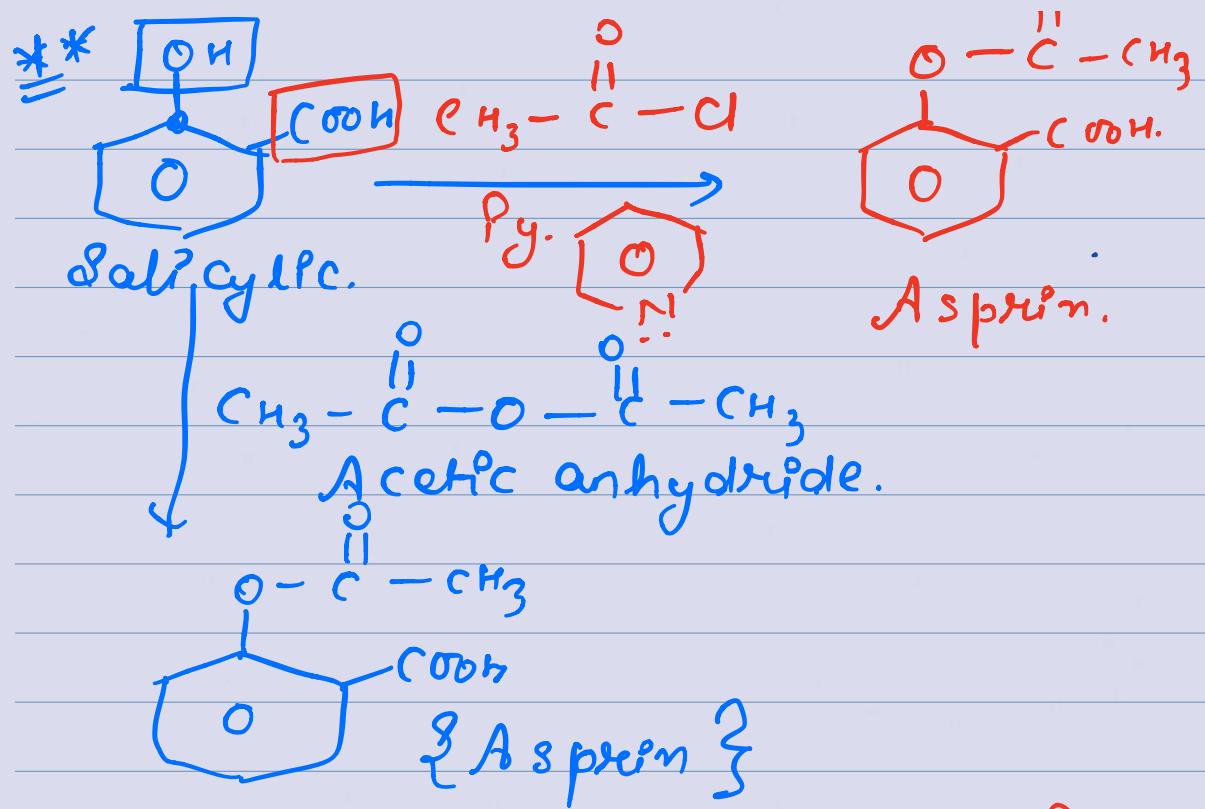
Mechanism :-



(Strong activator)

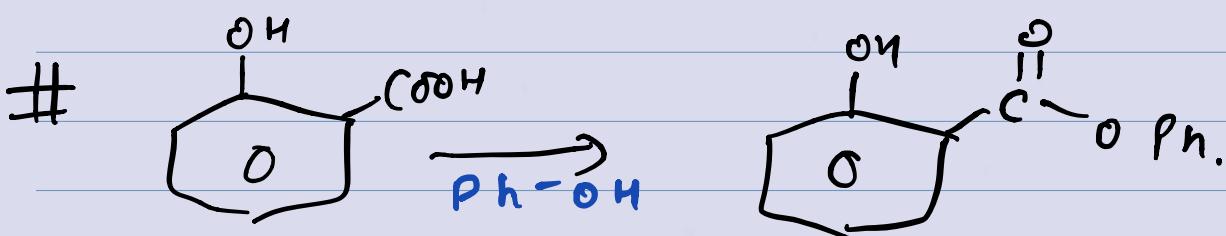






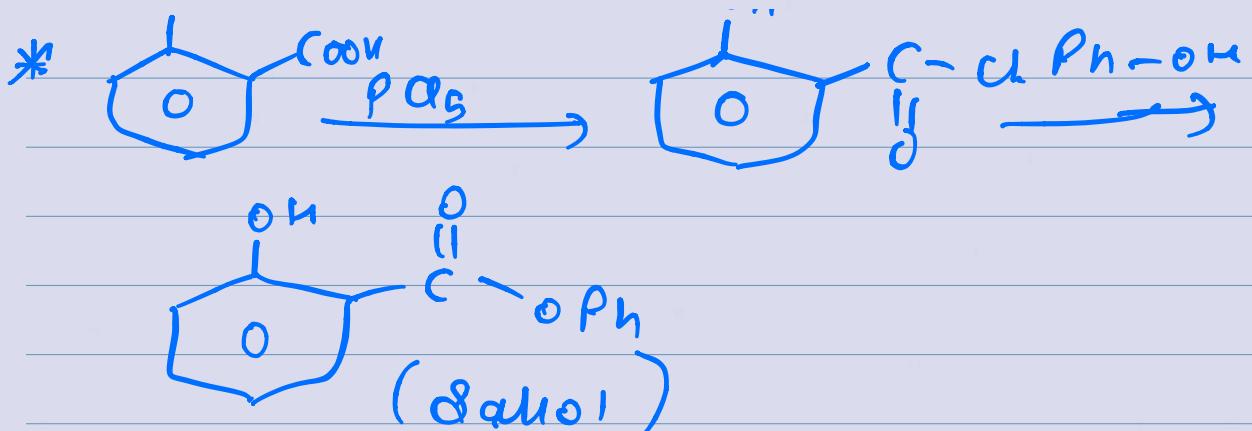
Salicylic acid.

Oil of winter green-  
(Iodex 8meli)

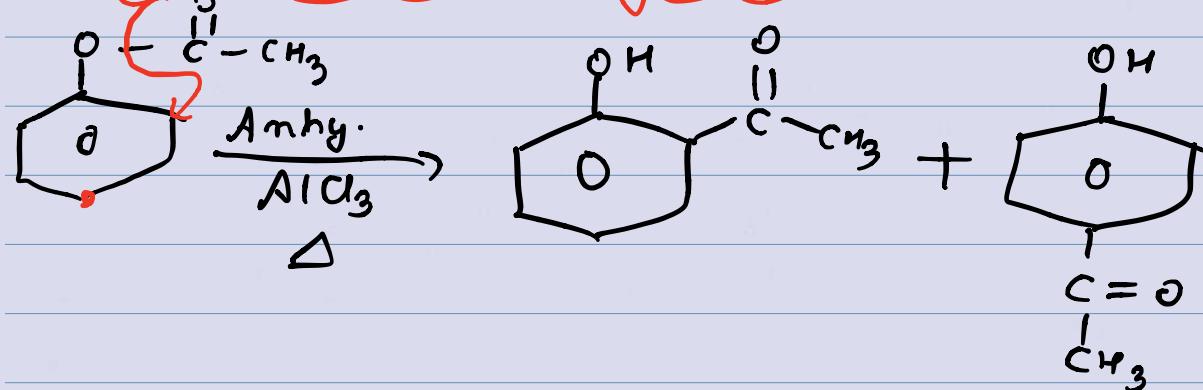


Salicylic acid.

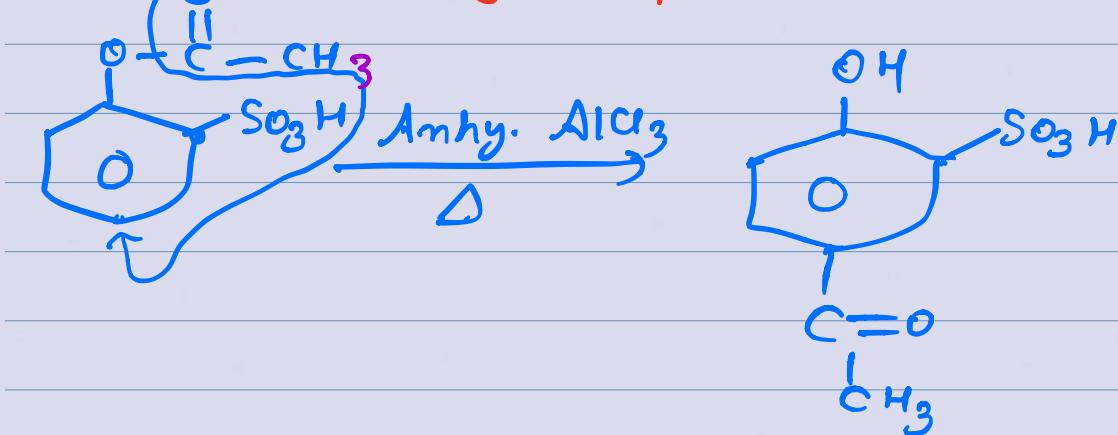
Salol.



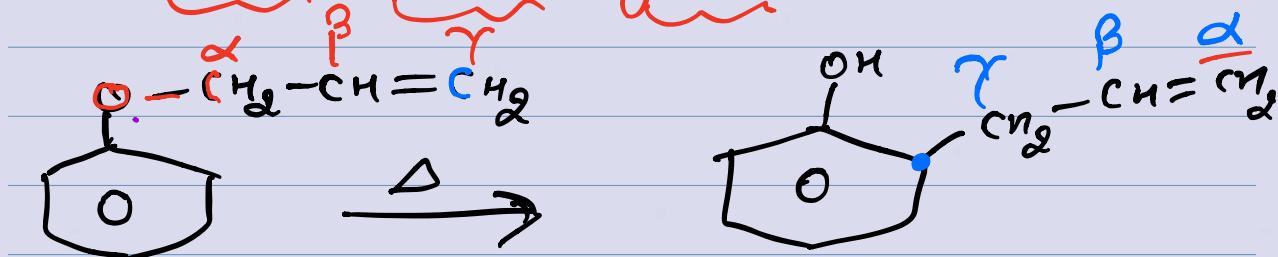
### # Frieds - Rearrangement $\ddot{\sigma}$



\* If one of the ortho position is already blocked then para substituted product will be our major product.

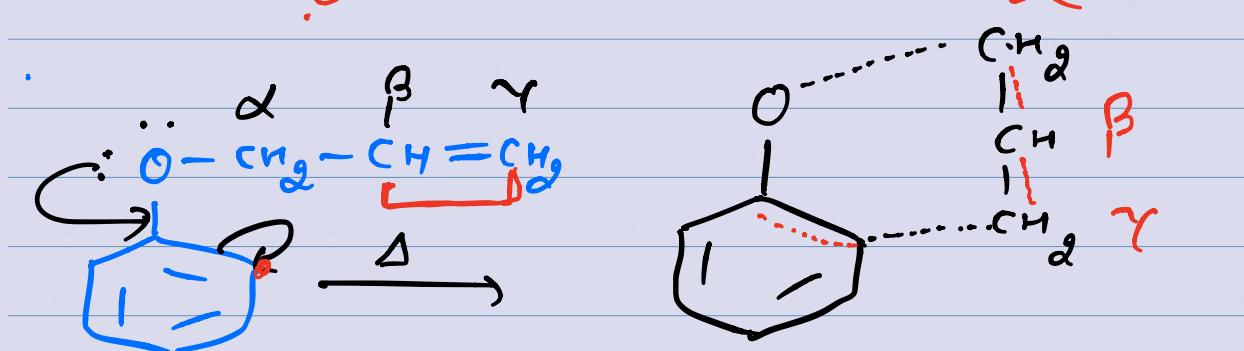


## # Claisen Rearrangement :-

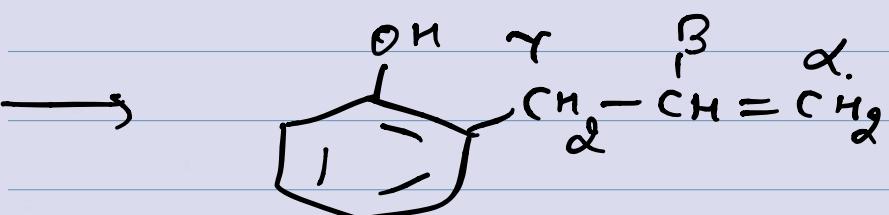


Allylic Phenylepic ethers.

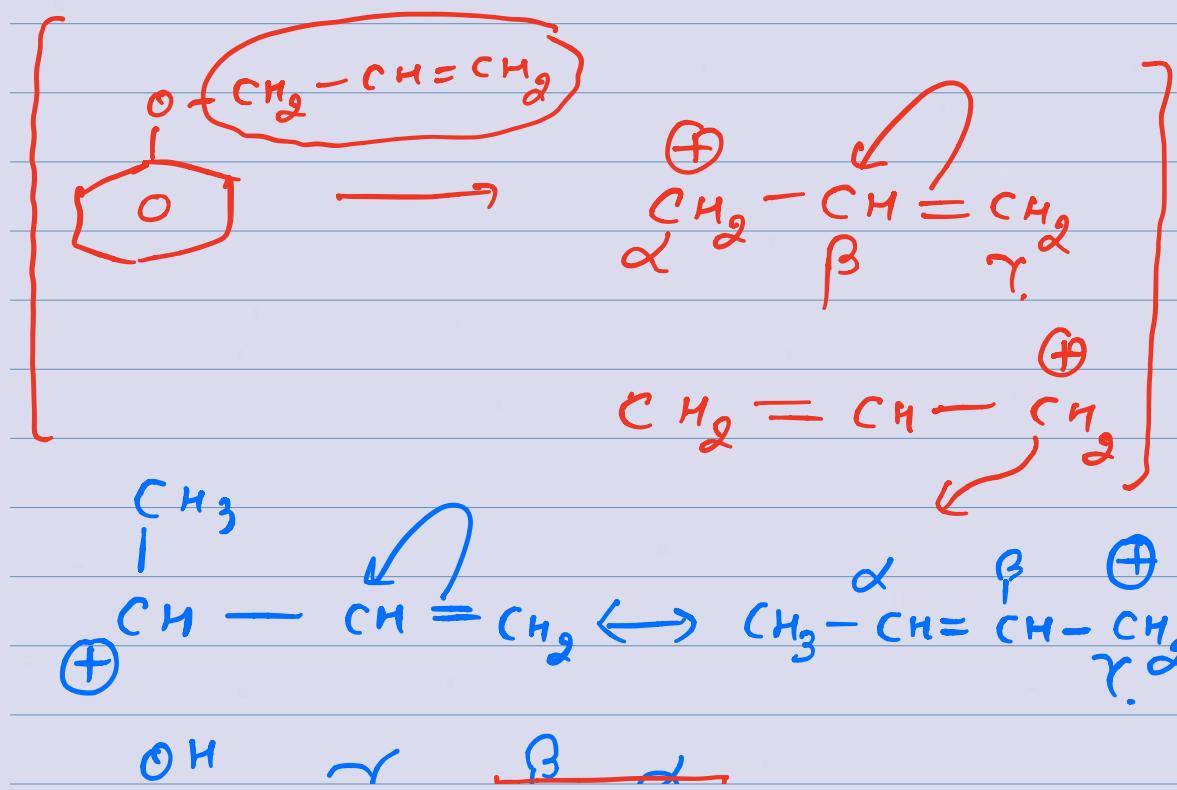
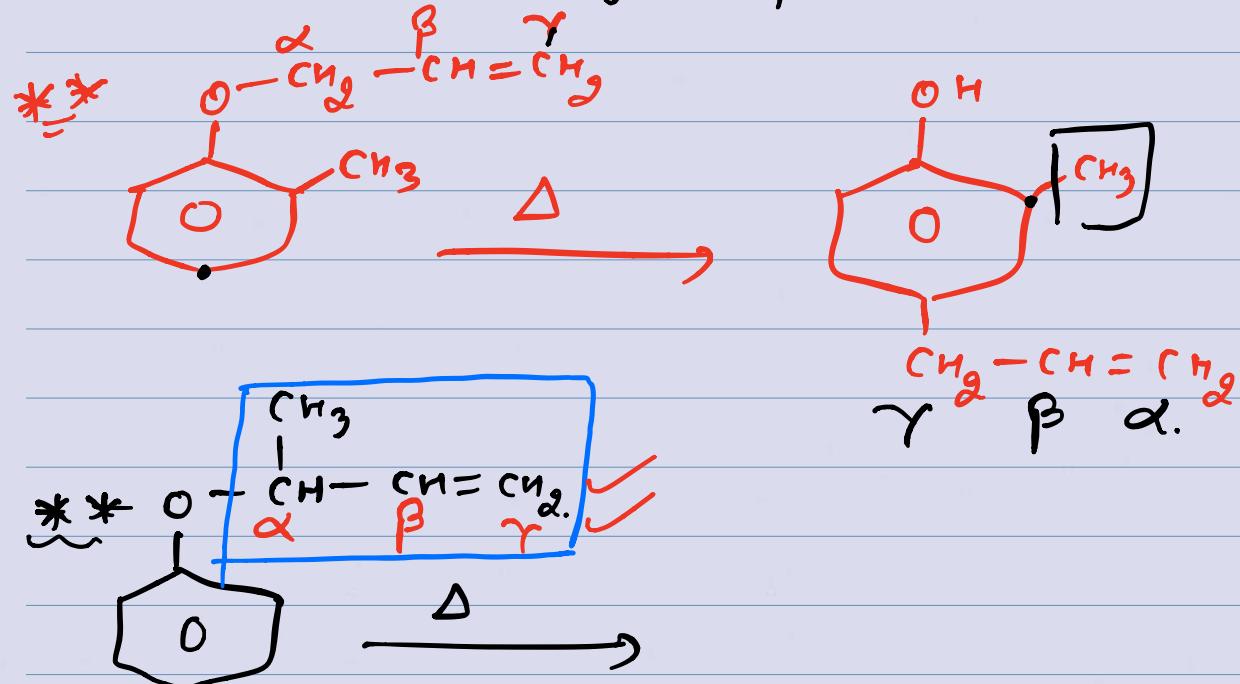
## Mechanism :-

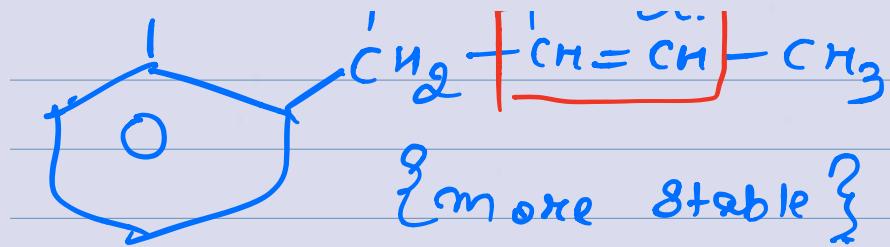


## Transition state.

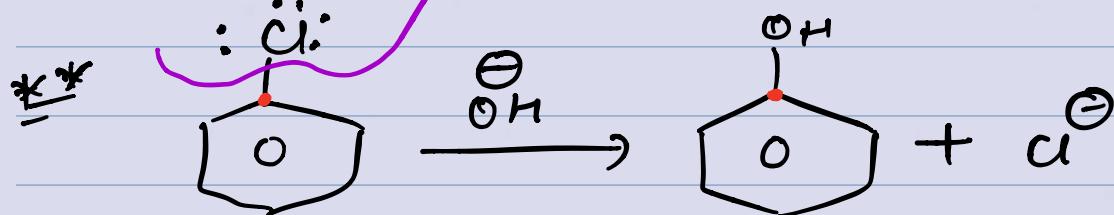


\*\* If one of the ortho position  
is blocked then Para product  
will be the major product.

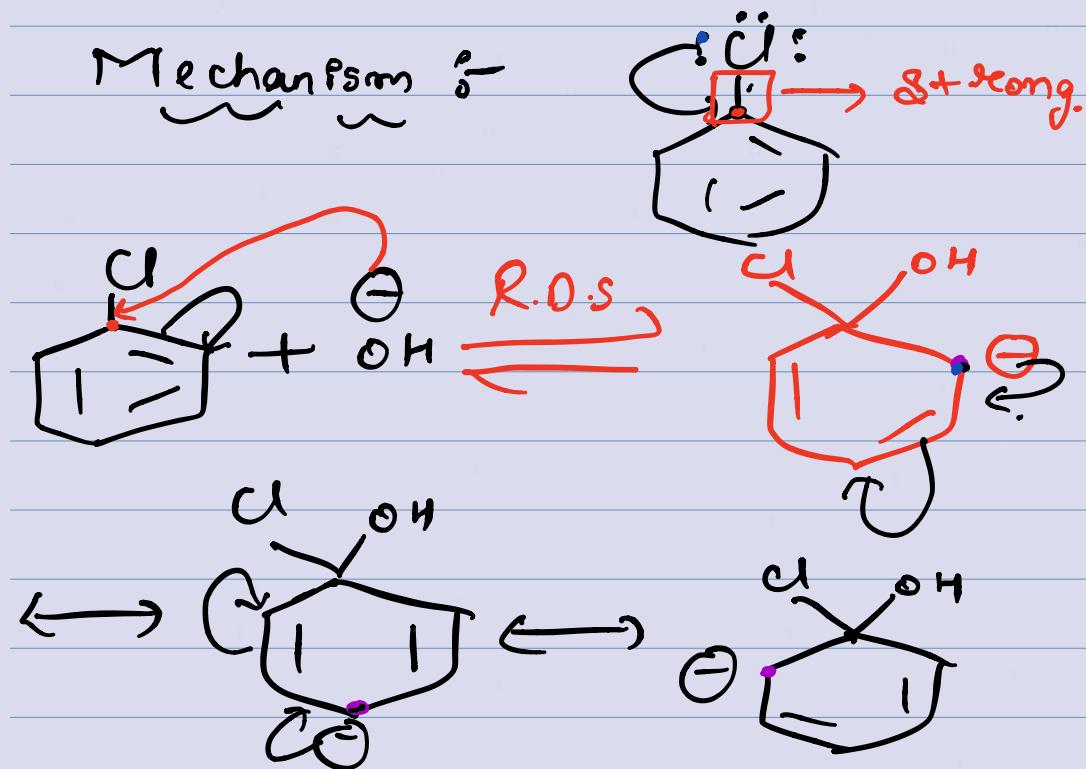




**# Aromatic Nucleophilic Substitution**  
 $\text{R}_x\text{n}^- \quad \text{ArSN}^2\}$

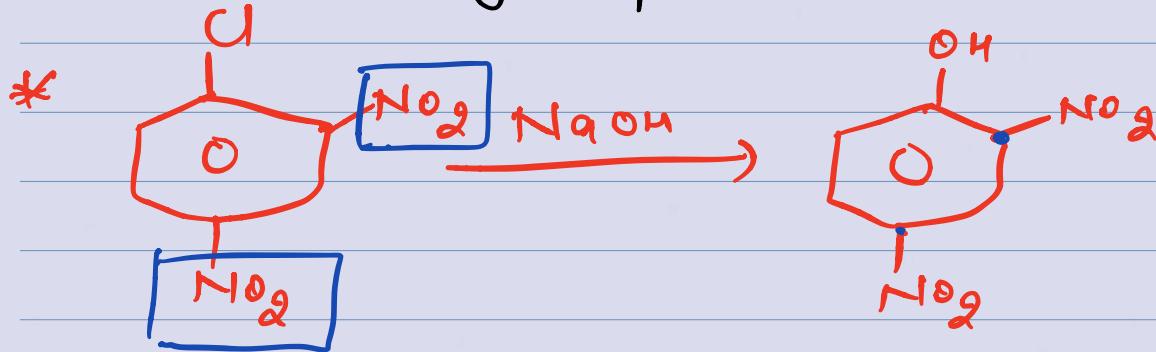


Mechanism

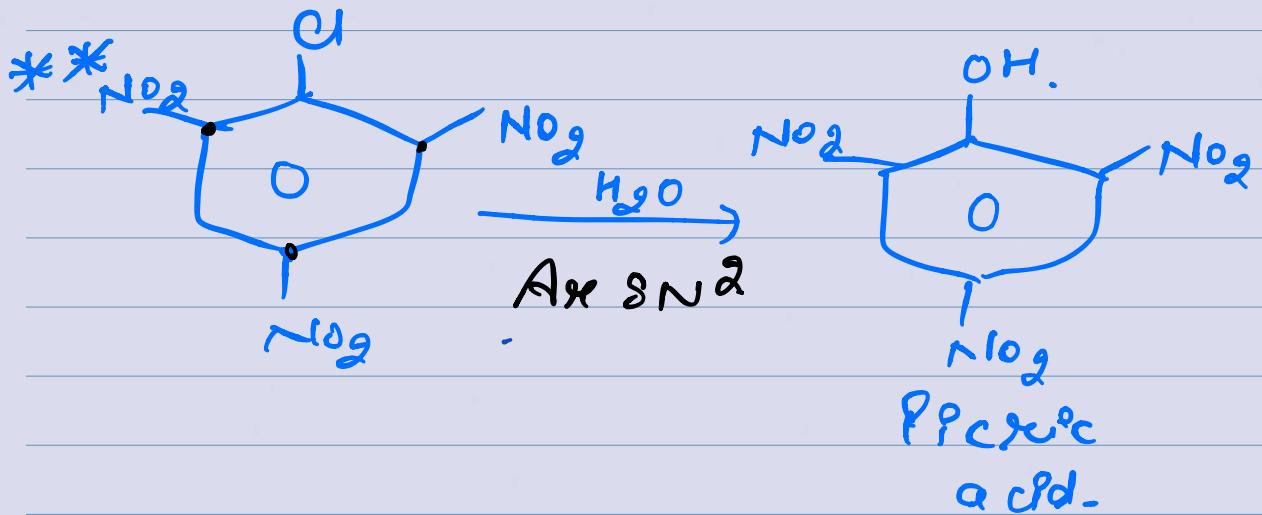


\* If E.W.G are attached at ortho or para position w.r.t. h. Gr.  
 then they will try to stabilize

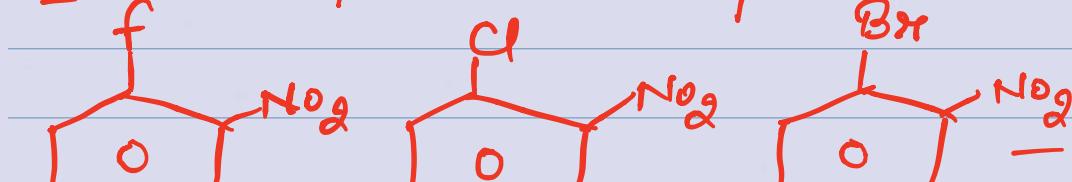
the -ve charge of benzene.

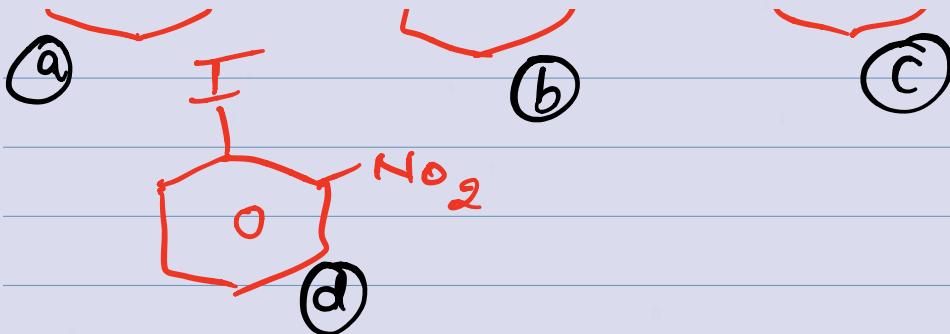


\* If ortho & Para positions are occupied by E.W.G then stability of anion will increase and hence rate of  $\text{Ar SNa}^2$  will also increase.

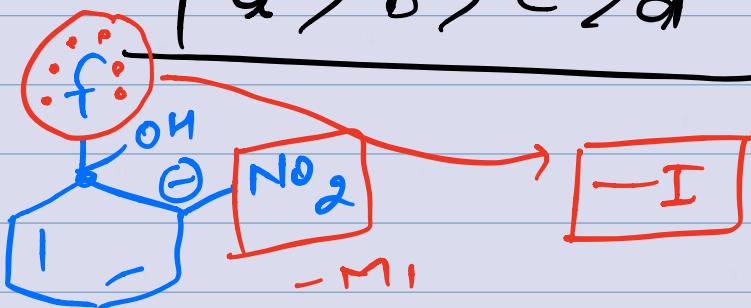


Ques:- Compare rate of  $\text{Ar SNa}^2$



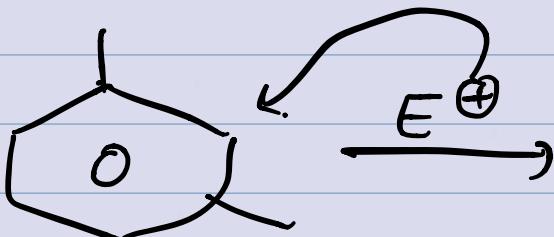


$$[a > b > c > d]$$

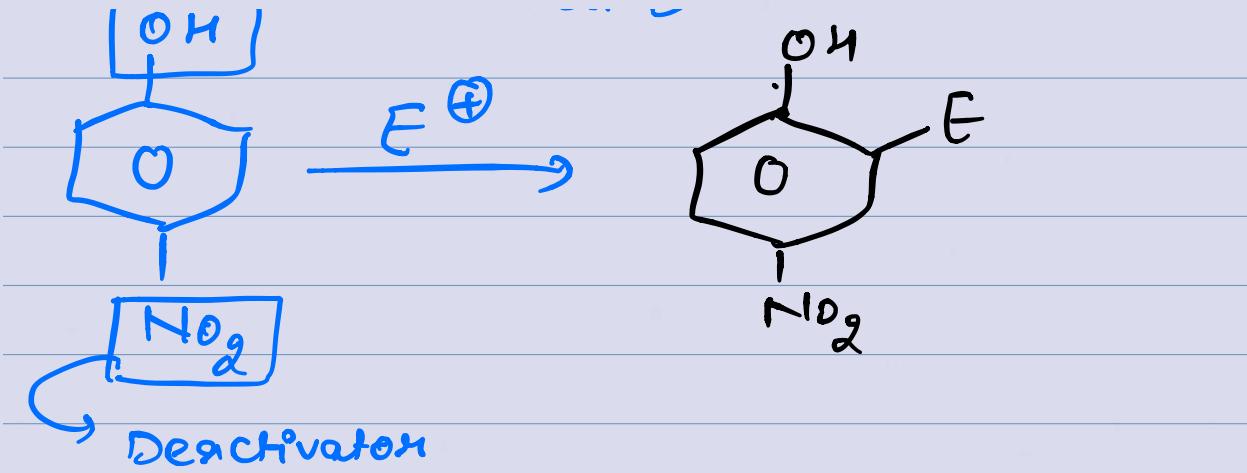


$$-I \rightarrow [f > a > b > I]$$

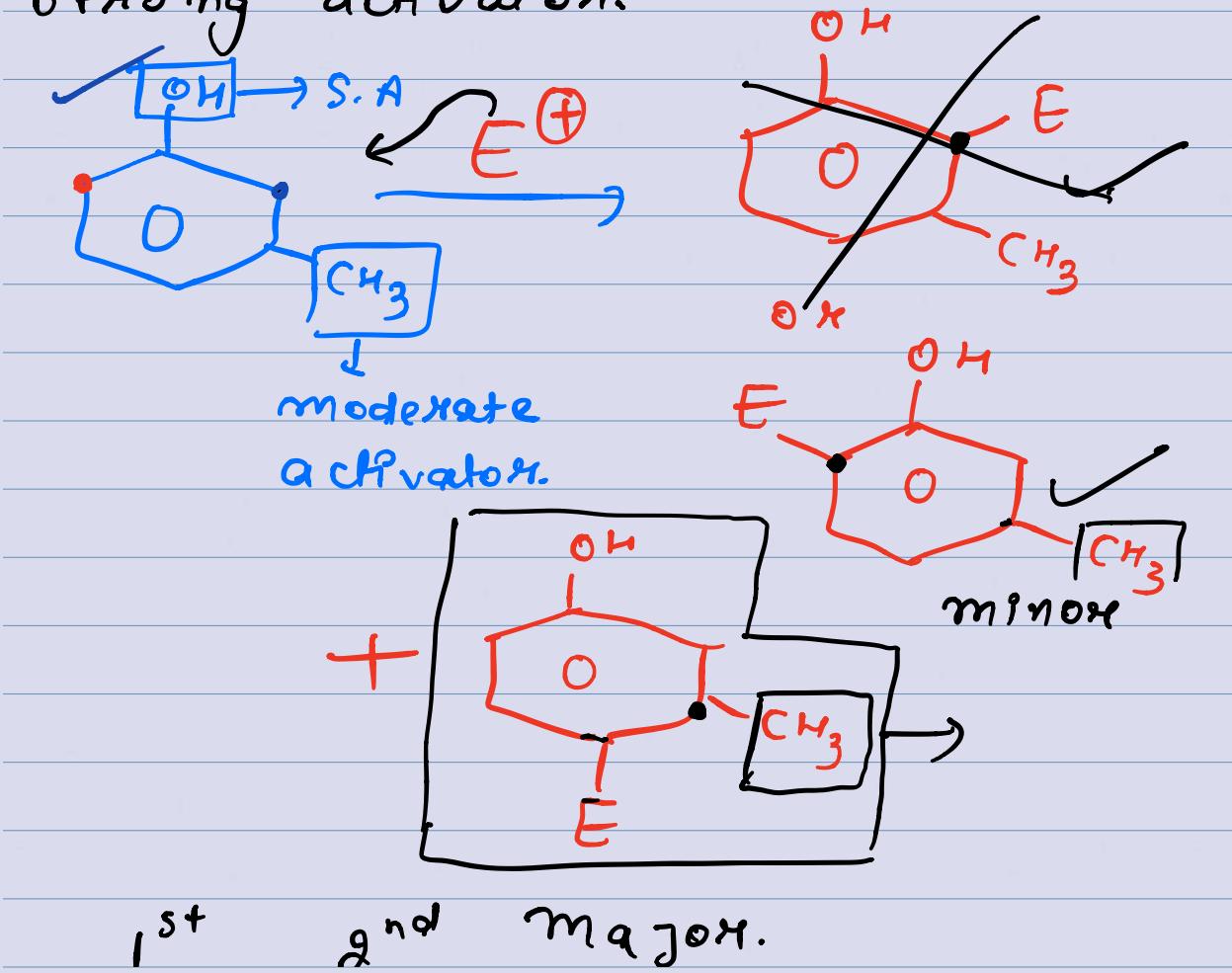
Electrophilic substitution rxns of  
disubstituted benzene

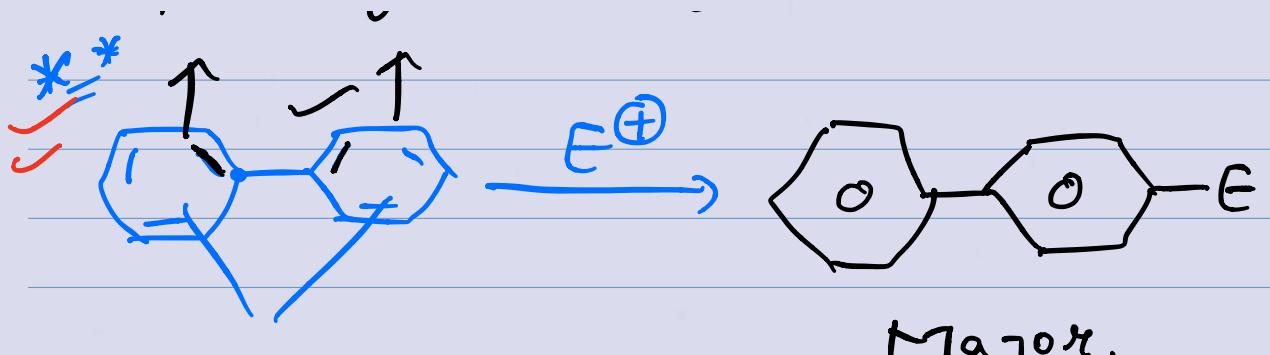


- 1) If one group is an activator and other group is deactivator then E.S.R takes place w.r.t. the activator.



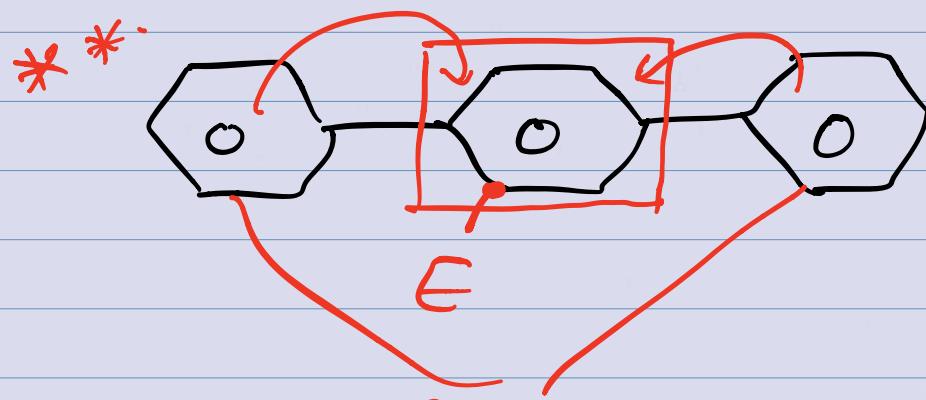
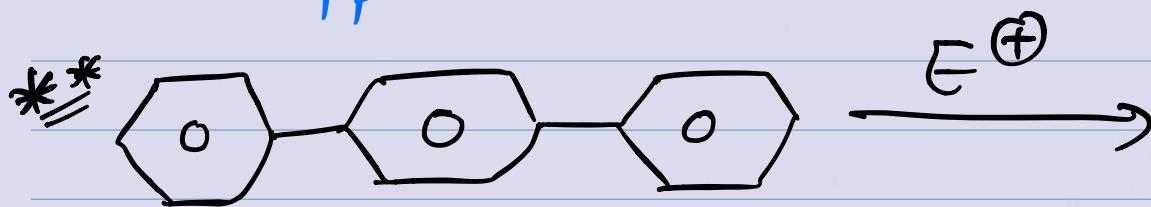
Q.) If one group is strong activator and other is moderate activator then E.S.R takes place w.r.t strong activator.





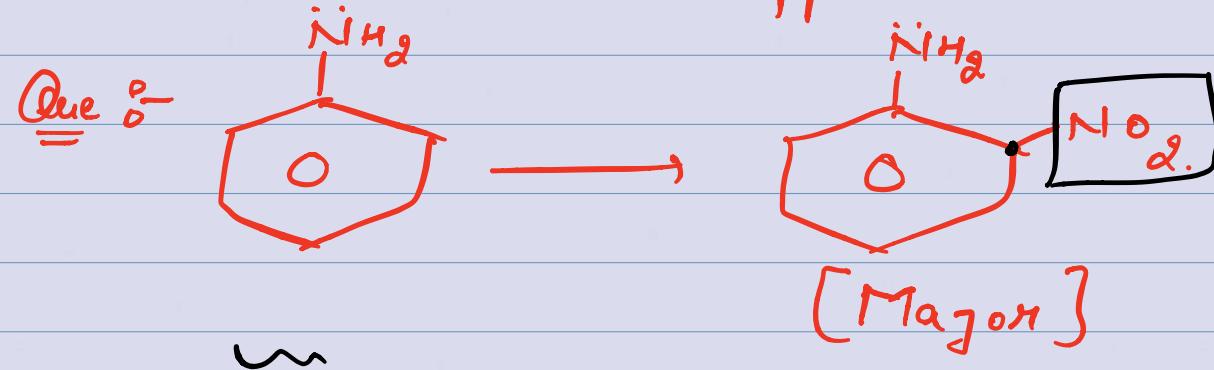
Major.

Both will show  
-M effect

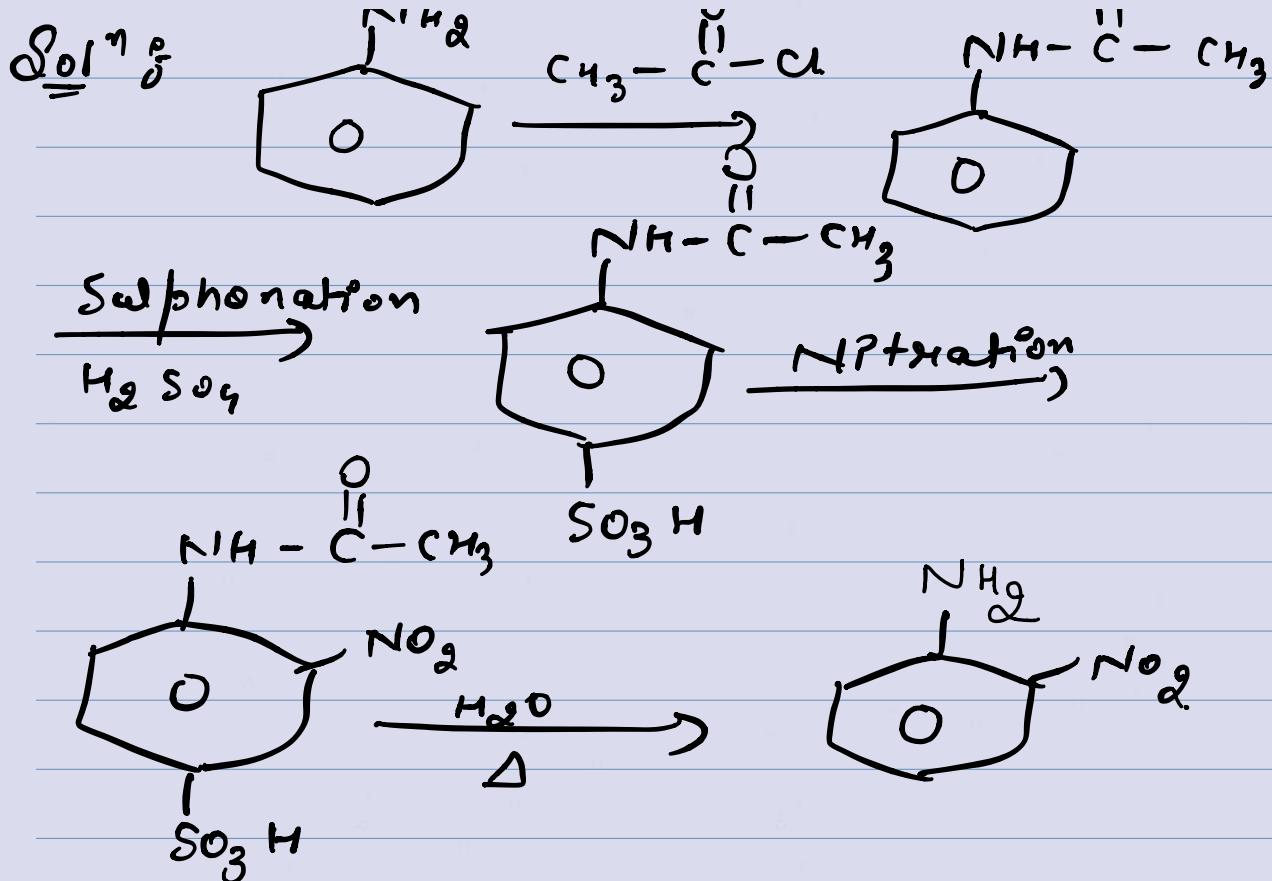


Both will show

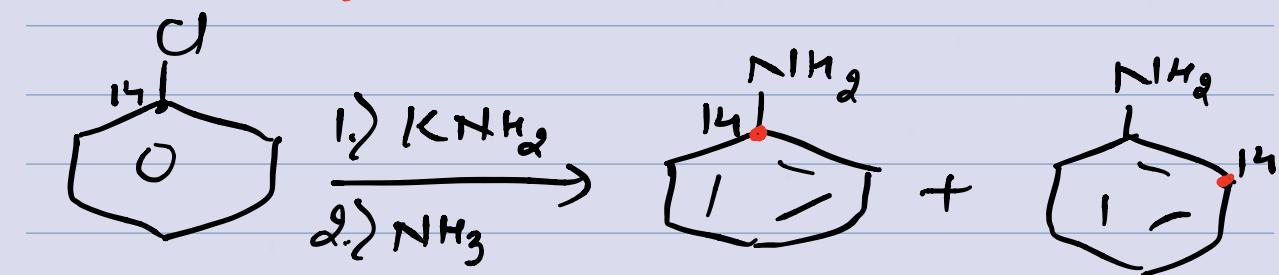
+M effect.



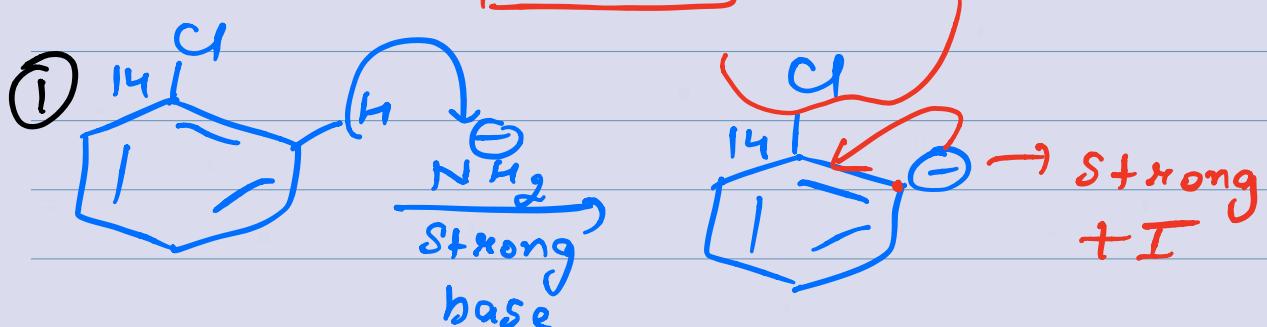
R



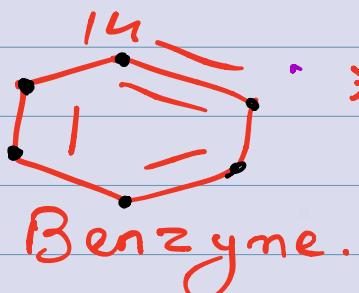
## # Benzene mechanism :-



Ans  $\text{ArSN}_2$  X Mechanism.

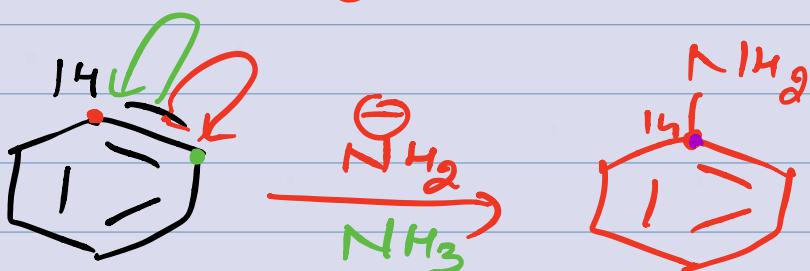


-Cl.



\* Benzyne is  
aromatic

②

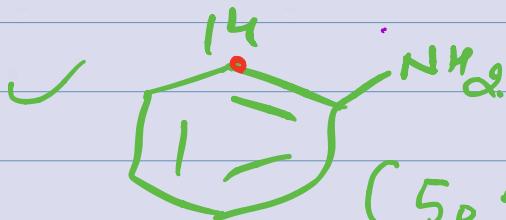


(50%)

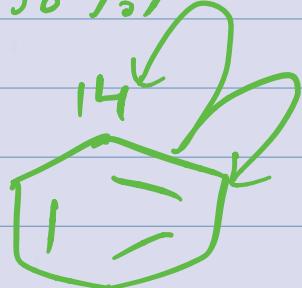


(50%)

Basic  
medium.



(50%)



50%  
Exper.

