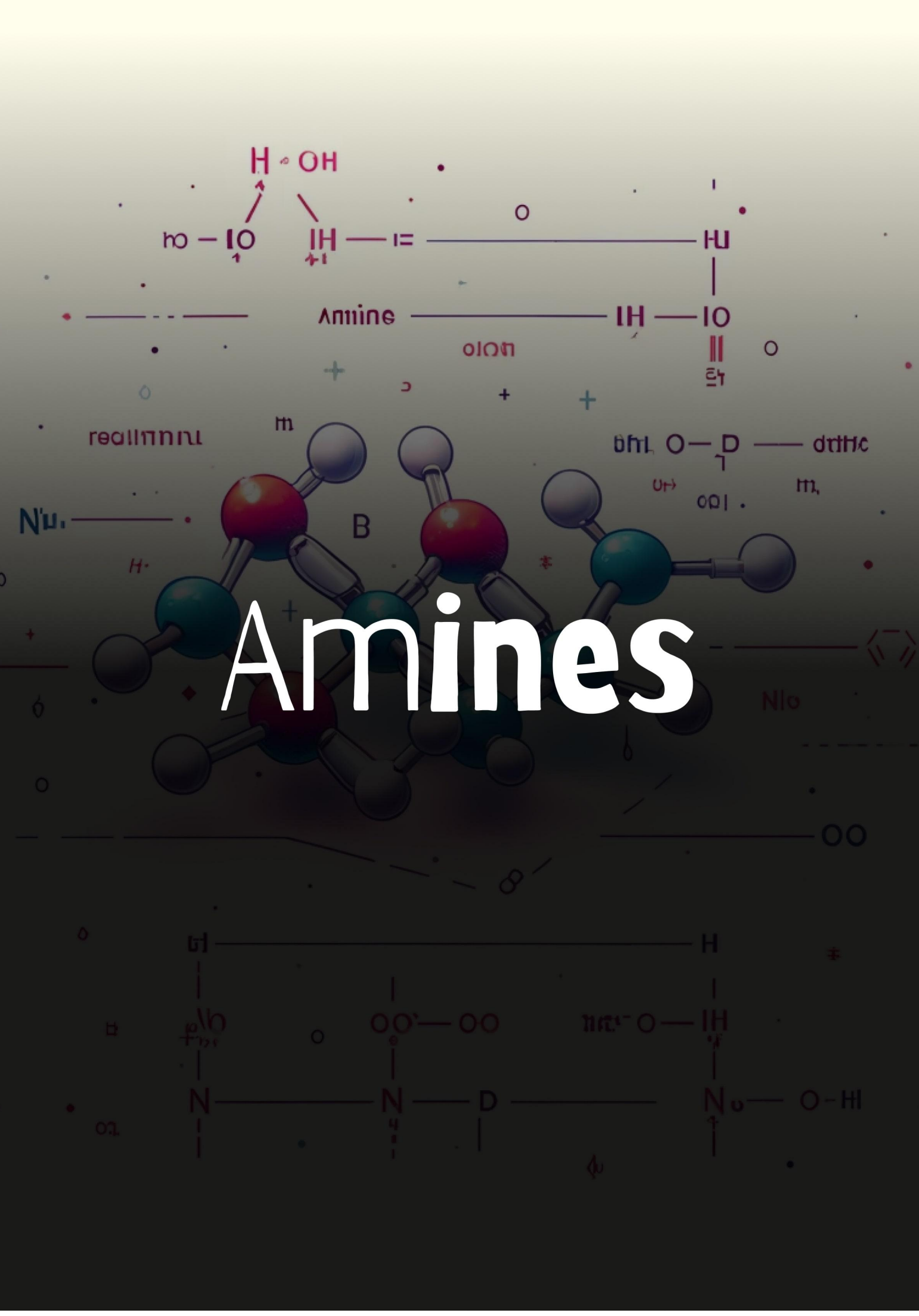


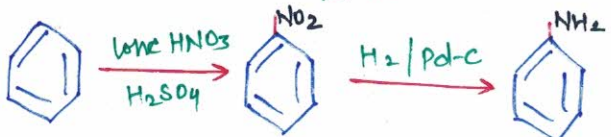
AMINES

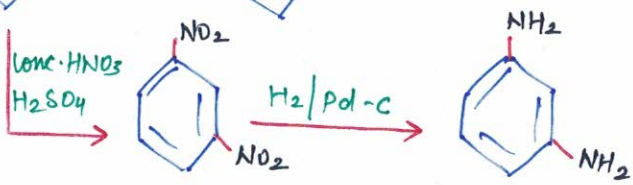
PREPARATION

@ FROM NITROCOMPOUNDS

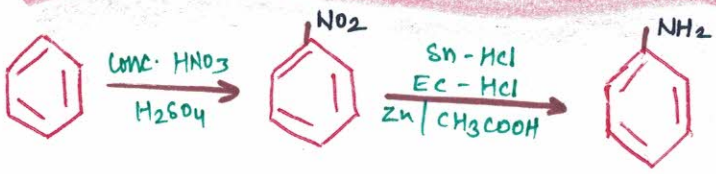
1. By Catalytic hydrogenation

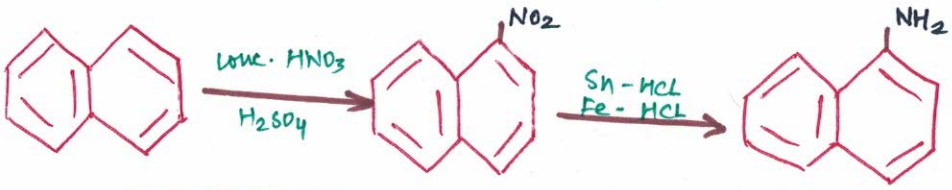
$$R-NO_2 + H_2 \xrightarrow[Pd-C]{Ni-C} R-NH_2$$



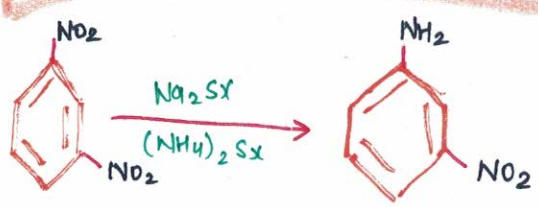


2. Reduction in acidic medium...

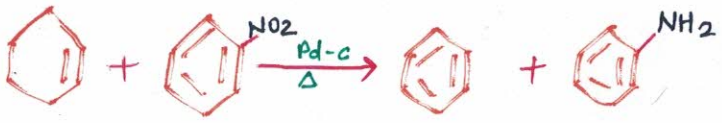




3. Reduction by $(NH_4)Sx$ / Na_2Sx

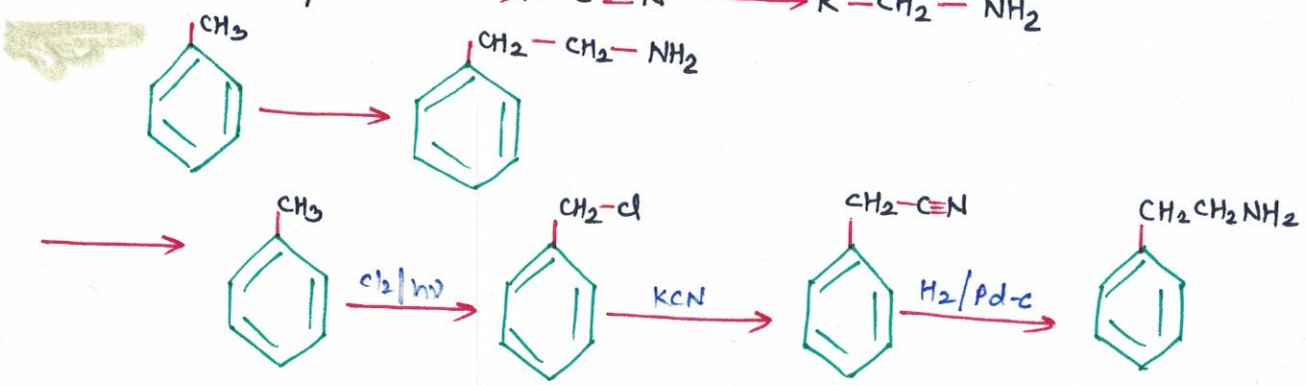


$$CH_3-CH_2-NO_2 \xrightarrow[Sn/HCL]{H_2/Ni-C} CH_3-CH_2-NH_2$$



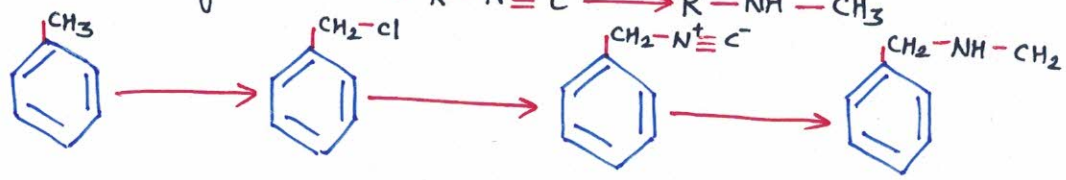
4. BY REDUCTION OF $RC\equiv N$

$$R-X + KCN/NaOH \longrightarrow R-C\equiv N \xrightarrow{H_2/Pd-C} R-CH_2-NH_2$$



BY REDUCTION OF ISOCYANIDES

$$R-X + AgCN \longrightarrow R-\overset{+}{N}\equiv\overset{-}{C} \xrightarrow{H_2\text{-}Pd\text{-}C} R-NH-CH_3$$

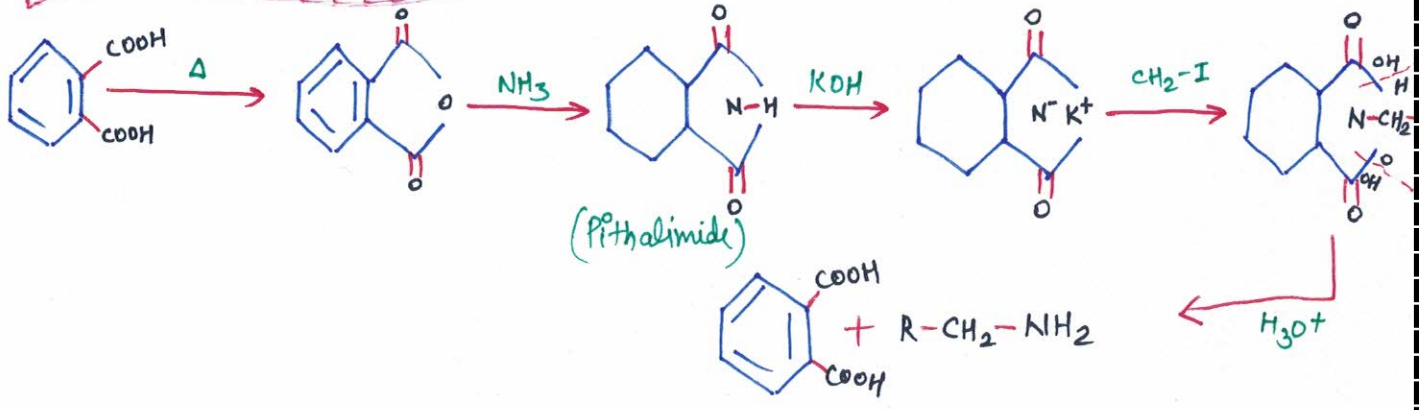


$$CH_3-CH_3 \longrightarrow CH_2=CH_2 \longrightarrow \underset{Br}{CH_2}-\underset{Br}{CH_2} \longrightarrow \bar{C}\equiv N^+-CH_2-CH_2-N^+\equiv C$$

$$\downarrow$$

$$CH_3-NH-CH_2-CH_2-NH-CH_3$$

GABRIEL SYNTHESIS

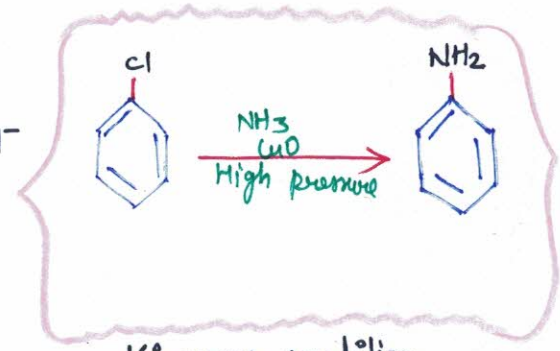


only primary alkyl amines can be prepared from gabriel synthesis.

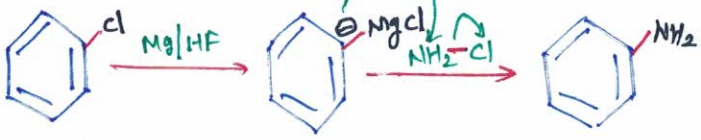
FROM GRIGNARD REAGENT

$R-X \xrightarrow[Et_2O]{Mg} R-MgX \xrightarrow{NH_2-Cl} R-NH_2 + Cl^-$

$R-MgX \xrightarrow{H-NH_2} R-H + NH_2^{\ominus}$



Rigorous condition

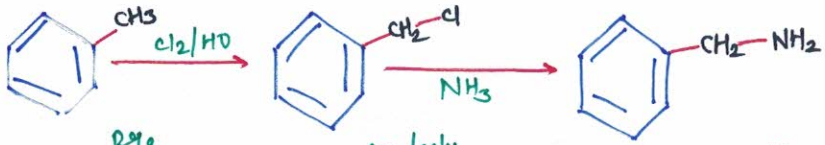
So, we use 

BY ALKYLATION OF AMMONIA / AMINE

$R-CH_2-I + NH_3 \longrightarrow R-CH_2-NH_2$

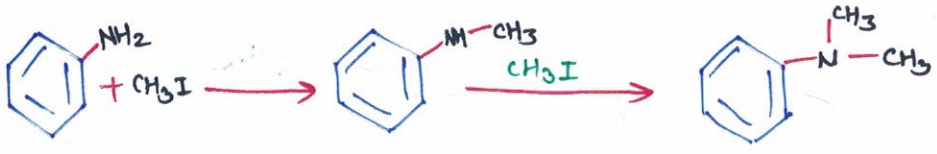
$CH_3-I + NH_3 \longrightarrow CH_3-NH_3^{\oplus}\,I^{\ominus} \longrightarrow CH_3-NH_2 + HI$

$CH_3CH_2Cl + NH_3 \longrightarrow CH_3CH_2NH_2 + HCl$

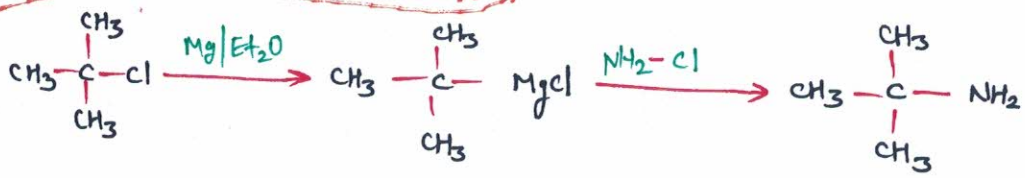


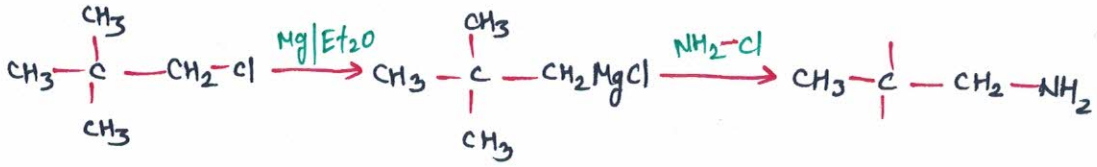
$CH_3-CH_3 \xrightarrow[Alc.KOH]{Br_2} CH_2=CH_2 \xrightarrow{Br_2/CCl_4} Br-CH_2-CH_2-Br \xrightarrow{2NH_3} H_2N-CH_2-CH_2-NH_2$

$CH_3CH_2NH_2 \xrightarrow{CH_3I} CH_3CH_2-NH-CH_3 \xrightarrow{CH_3I} CH_3CH_2-\overset{CH_3}{\underset{|}{N}}-CH_3 \xrightarrow{CH_3I} CH_3CH_2-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^{\oplus}}}}}-CH_3$



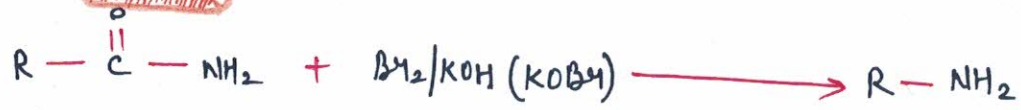
GRIGNARD CONTINUED !!!



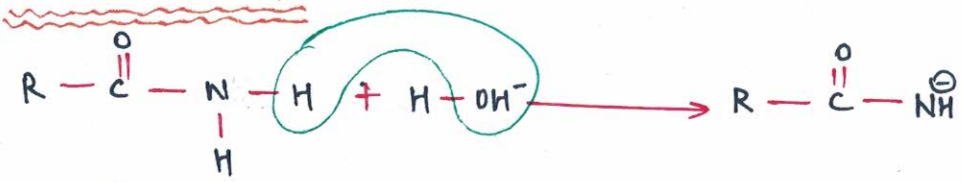


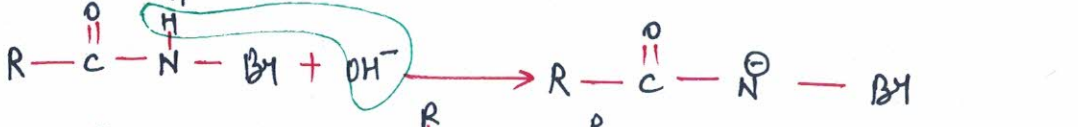
Those amines which cannot be prepared by alkylation or any method, can be prepared by grignard reagent.

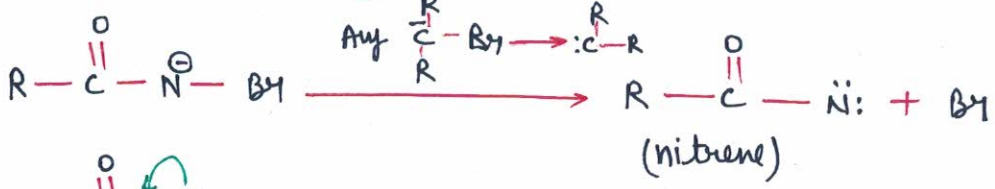
HOFFMAN HYPOBROMIDE REACTION



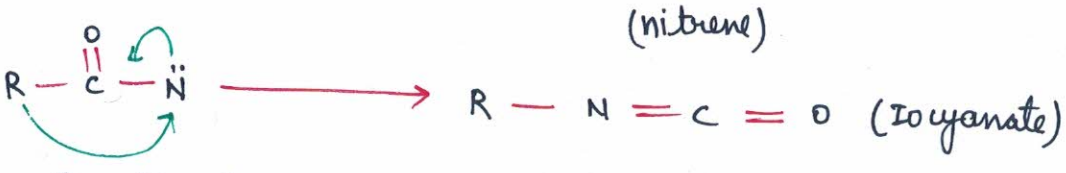
MECHANISM

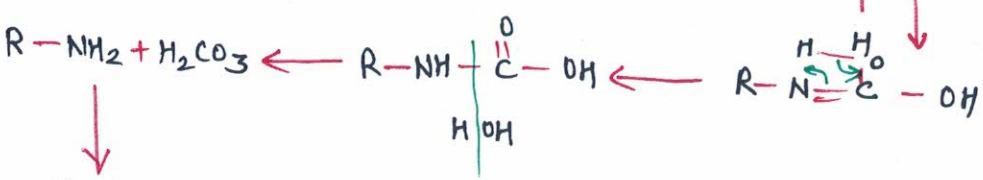


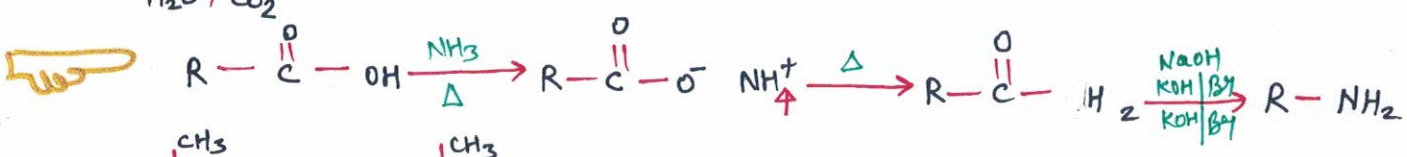


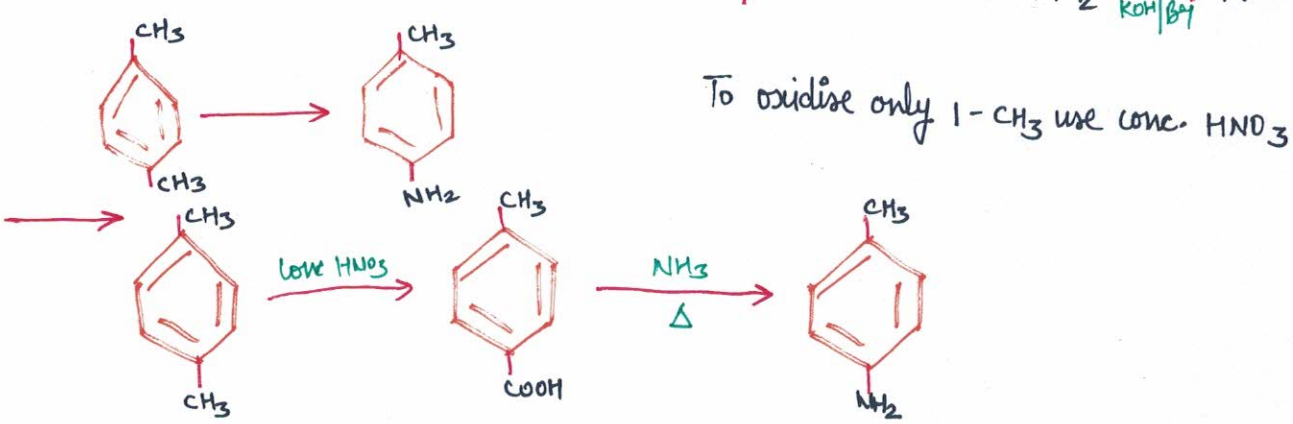


(nitrene)

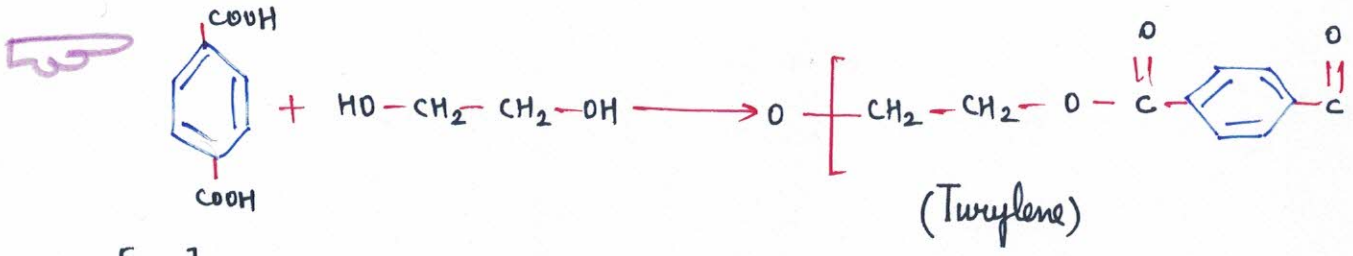






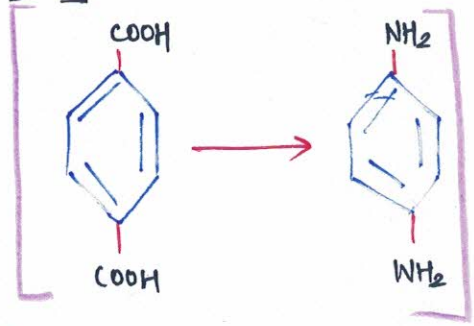


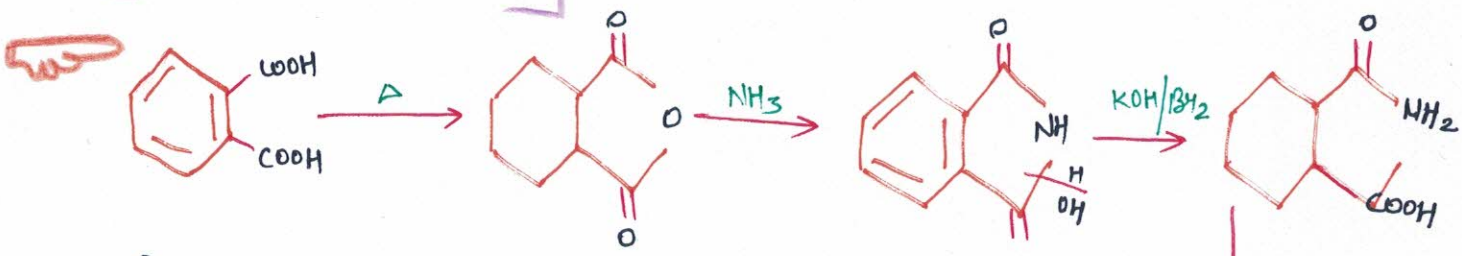
To oxidise only 1-CH_3 use conc. HNO_3

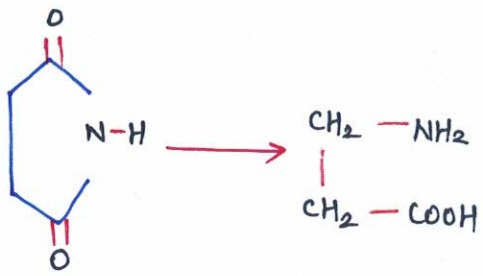


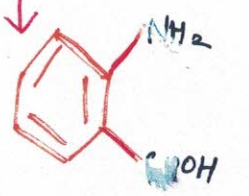
(Terylene)

[PET]

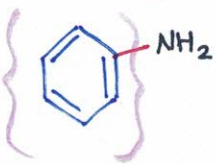








PROPERTIES OF AMINES

- Reaction due to $-NH_2$ — $R-NH_2$
- Reaction due to ring — 

REACTION DUE TO AMINE GROUP

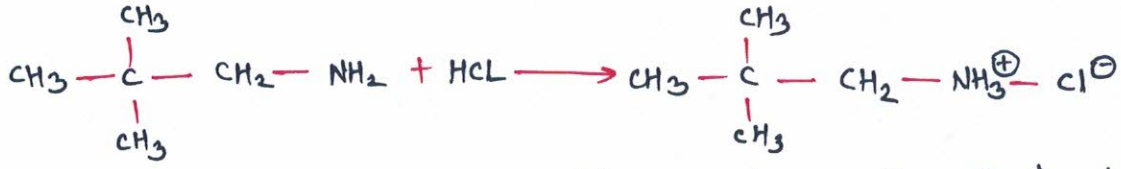
1. SALT FORMATION

(base) (acid)

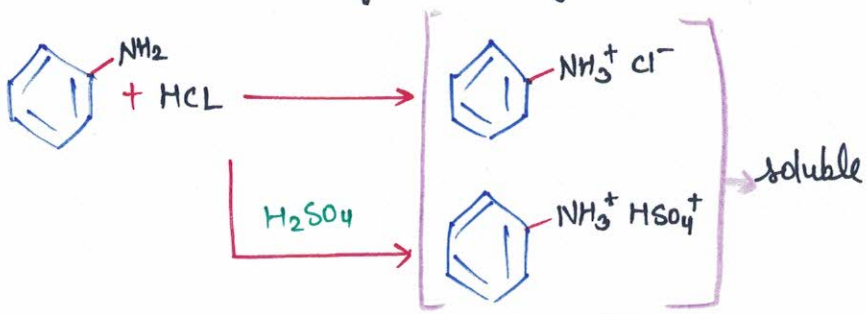
$R-NH_2 + HCL \longrightarrow R-NH_3^{\oplus}\,Cl^{\ominus}$

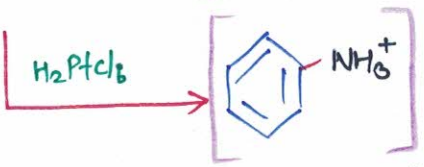
$R_1-NH(R_2) + HCL \longrightarrow R_1-NH_2^{\oplus}(R_2)\,Cl^{\ominus}$

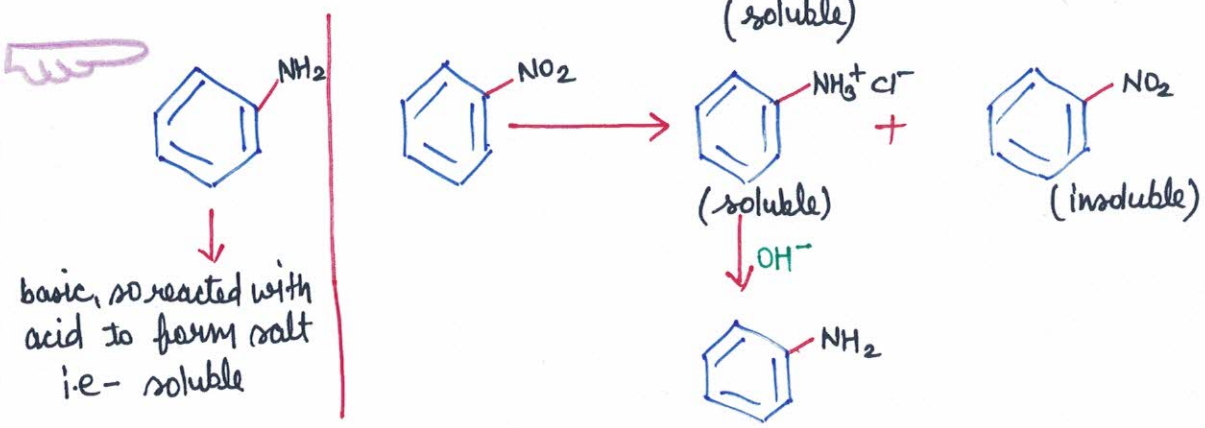
E.g.



Salts are ionic so salts are more soluble in water. Amilene is insoluble in water. Freshly distilled amilene is clear like water but after few hours it appears brown due to oxidation due to high e^- density in ring.

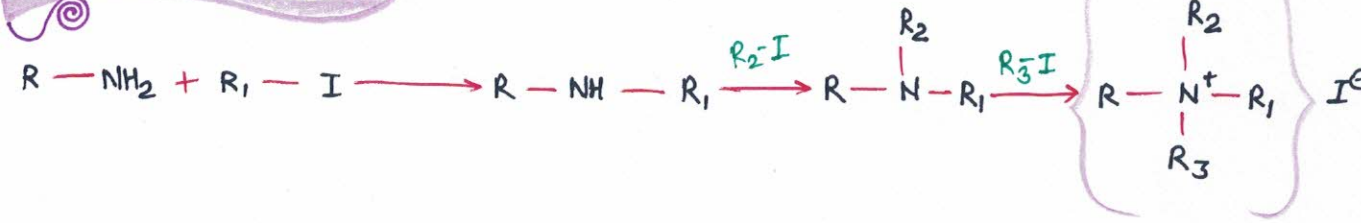






We can separate an acid and basic compound by using either acid or basic and we can separate acidic & neutral by using base and basic & neutral by using acidic as salt is formed which is soluble and hence can be easily separate from water layer.

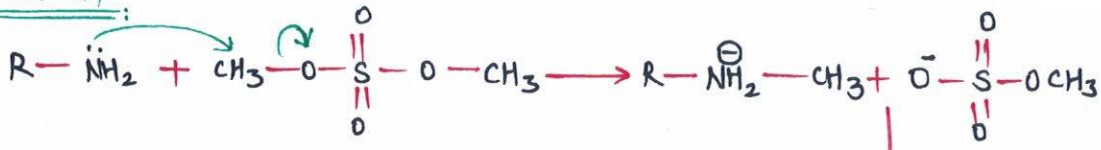
2. ALKYLATION

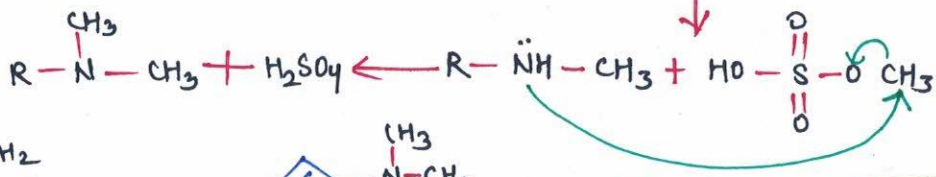


3. REACTION WITH $(CH_3)_2SO_4$ (Dimethyl sulphate)

$$R-NH_2 + (CH_3)_2SO_4 \longrightarrow R-\overset{CH_3}{\underset{|}{N}}-CH_3 + H_2SO_4$$

MECHANISM





$$Z-NH_2 \xrightarrow{(CH_3)_2SO_4} Z-\overset{CH_3}{\underset{|}{N}}-CH_3$$

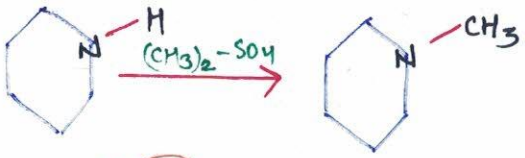
$$Z-OH \xrightarrow{(CH_3)_2SO_4} Z-O-CH_3$$

Di methyl sulphate is a methylating agent.

$$Z-\overset{O}{\overset{||}{C}}-OH \xrightarrow{(CH_3)_2SO_4} Z-\overset{O}{\overset{||}{C}}-O-CH_3$$

$$HO-\overset{O}{\underset{O}{\overset{||}{S}}}-OH \;>\; CH_3-O-\overset{O}{\underset{O}{\overset{||}{S}}}-OH \;>\; CH_3-O-\overset{O}{\underset{O}{\overset{||}{S}}}-O-CH_3 \text{ (Viscosity)}$$

Therefore, $CH_3-O-\overset{O}{\underset{O}{\overset{||}{S}}}-O-CH_3$ has high volatility. So, we inhale it as it has no smell and it goes into our lungs, hydrolyses in our lungs. H_2SO_4 is formed and our lungs get punctured. Hence, it is highly dangerous.

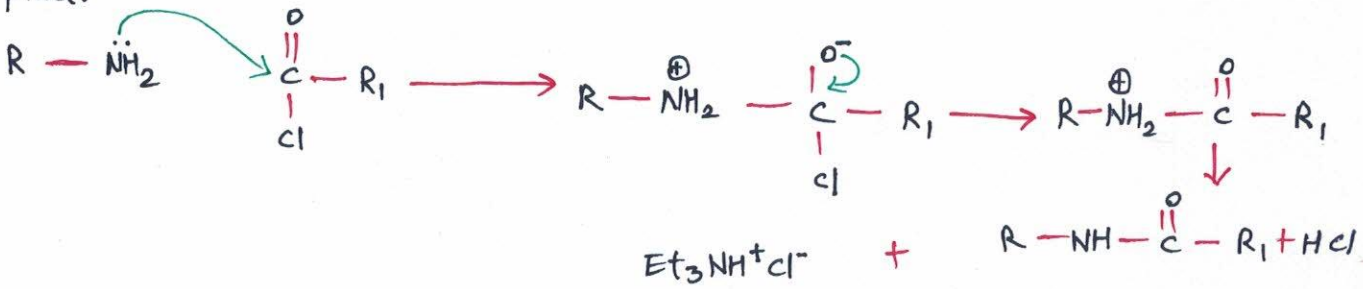


4. ACYLATION

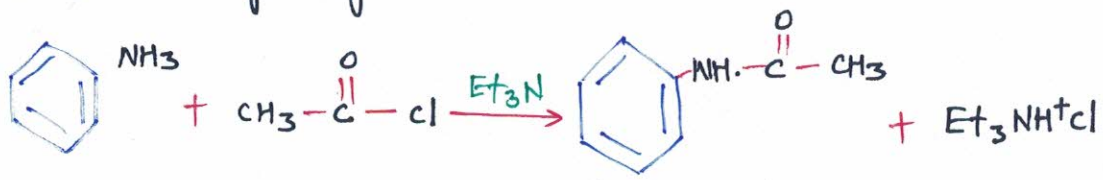
$$R-NH_2 + R_1-\overset{O}{\overset{||}{C}}-Cl \xrightarrow[\text{Pyridine}]{Et_3N,\ Me_3N} R-NH-\overset{O}{\overset{||}{C}}-R_1 + Et_3NH^+Cl^-$$

(a tertiary amine)

The catalysts act as acid absorbens so that backward reactions does not take place.

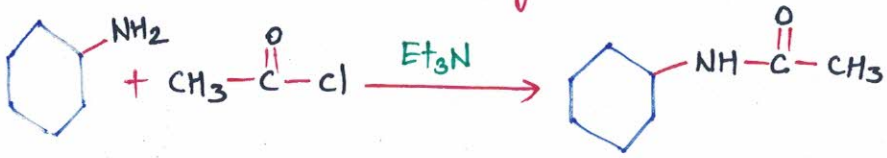


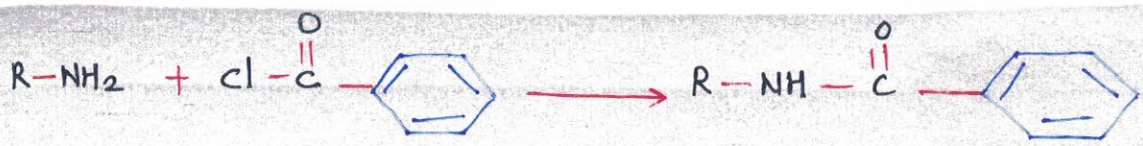
only primary & secondary amines undergo acylation Tertiary amines do not undergo acylation.

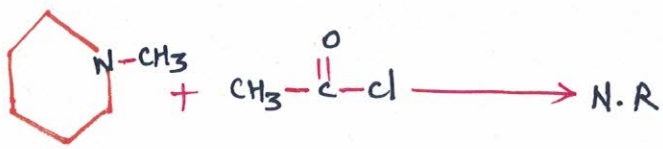


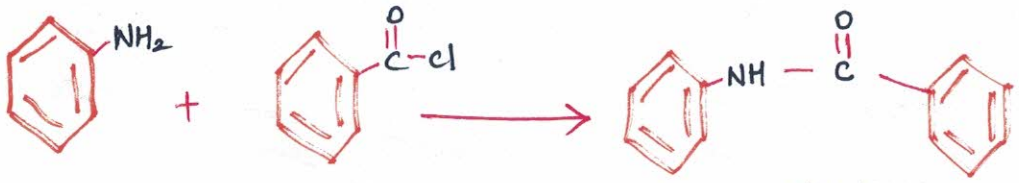
(Acetanilide)
(n phenyl methanamide)

This process is called acetylation.



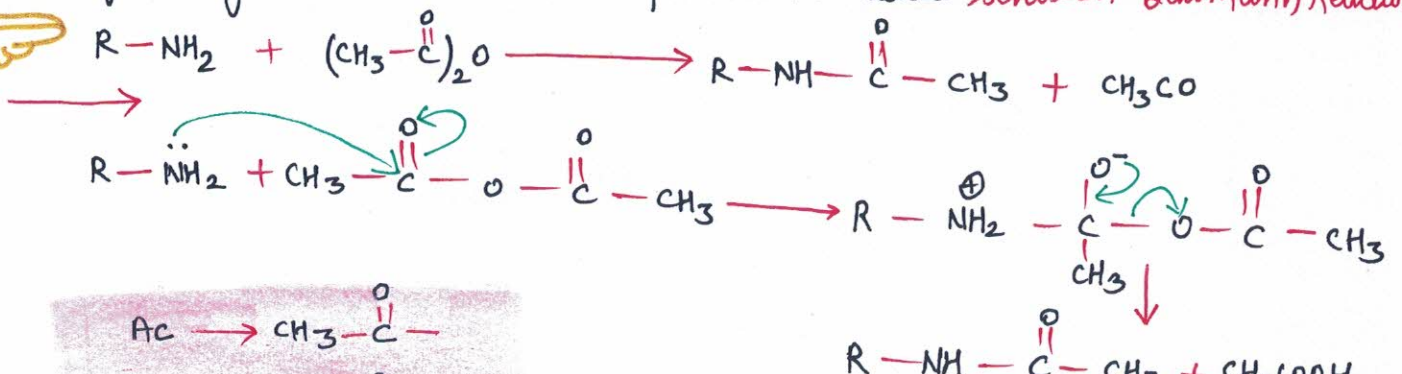






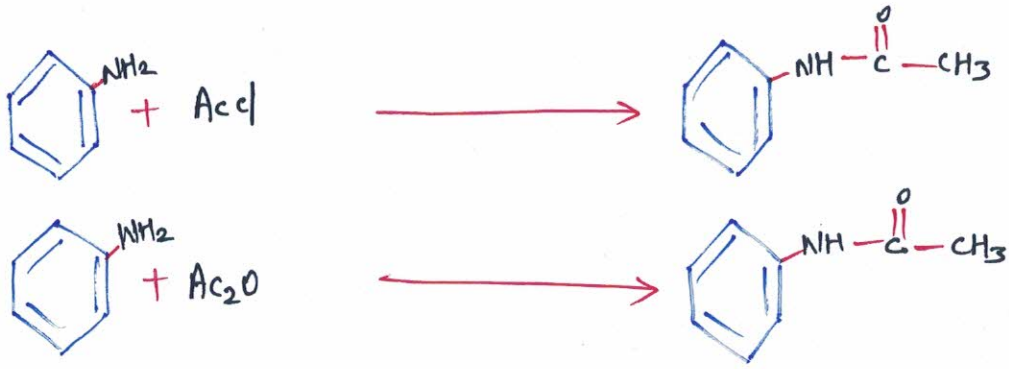
(Benzanilide)
{n phenyl benzacarbamide}

Benzoylation of aromatic amines & phenols is called "Schotten Baumann Reaction."



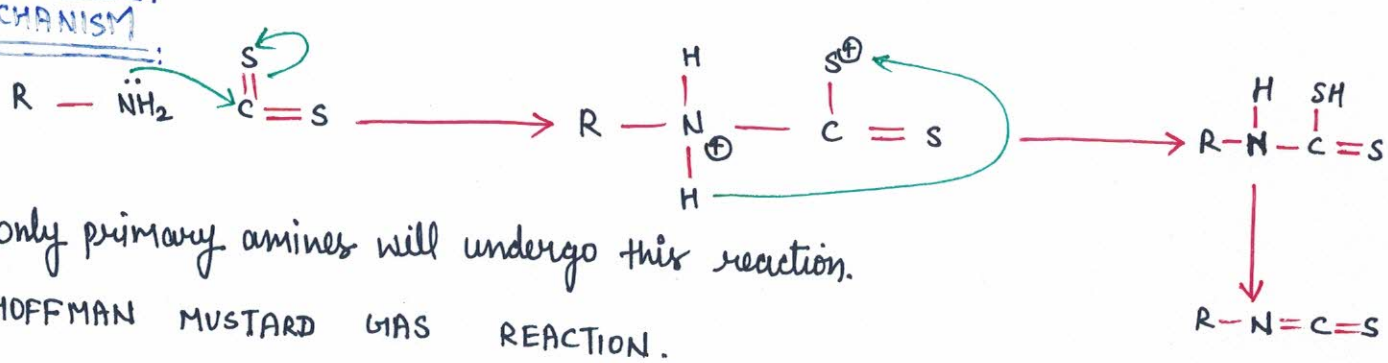
Ac → $CH_3-C(=O)-$

Accl → $CH_3-C(=O)-Cl$



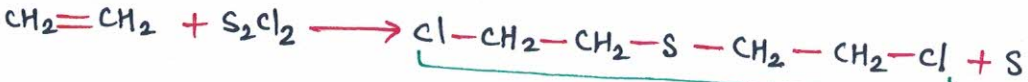
HOFFMAN MUSTARD OIL REACTION

MECHANISM



Only primary amines will undergo this reaction.

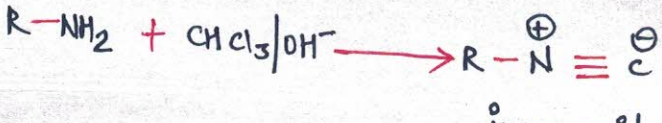
HOFFMAN MUSTARD GAS REACTION.



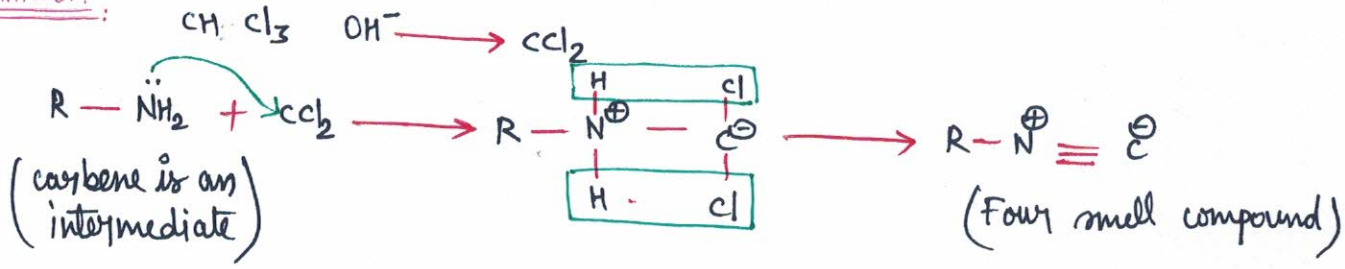
It easily undergoes hydrolysis due to anchimeric assistance.

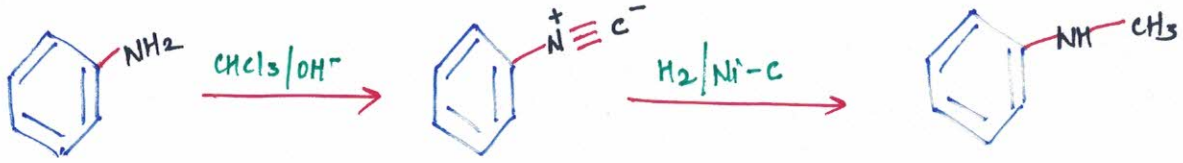
CARBYL AMINE REACTION

Also called Hoffman isocyanide reaction or carbyl amine test.

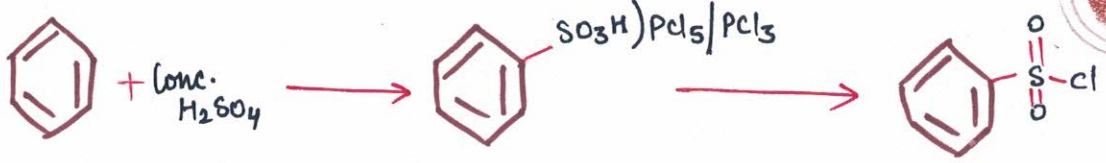


MECHANISM





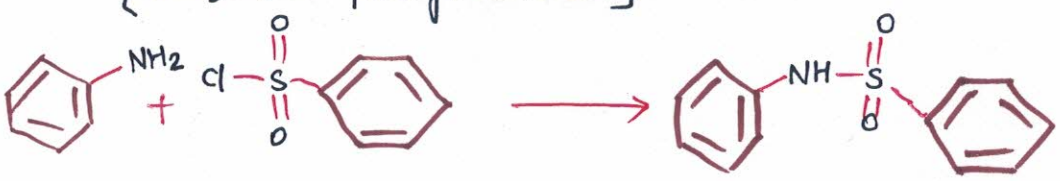
Reaction with HENSBURG Reagent



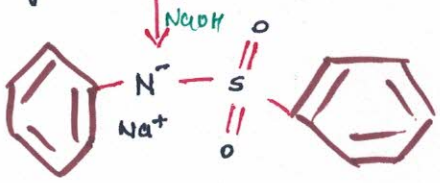
$Ph-SO_2-Cl$ is called "Hensburg reagent."

↓

{Benzene sulphonyl chloride}

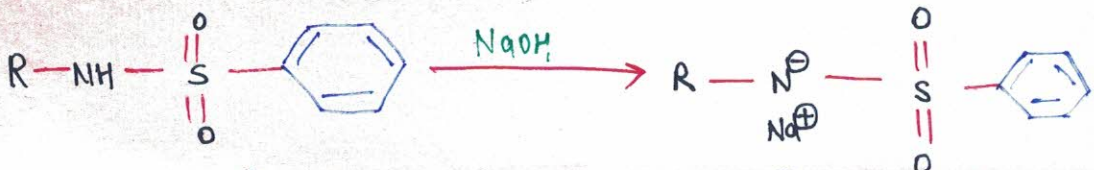


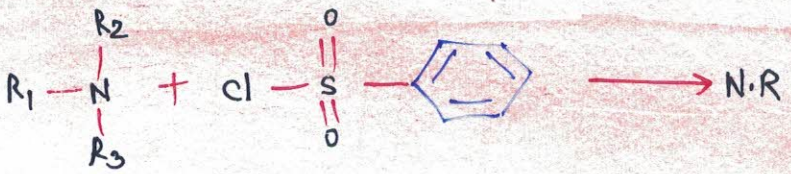
(White crystalline product)



(soluble in NaOH)

Amines	neutral
Imides	acidic
sulphamides	more acidic





Ensburg reagent is used to distinguish and separate primary, secondary & tertiary agent.

Primary amine	white ppt & soluble in NaOH
Secondary amine	only white ppt & insoluble
Tertiary amine	No white ppt.

Reaction with HNO_2 ($NaNO_2/HCl$)

a. **WITH PRIMARY AMINE** - HNO_2 is unstable so we generate it by $NaNO_2 + HCl$ and use it simultaneo-usly.

$$R\,NH_2 / Ar\,NH_2 \xrightarrow[NaNO_2/HCl]{HNO_2} R-N\equiv N^+\,Cl^- \quad / \quad Ar-N\equiv N^+\,Cl^-$$

The process of converting primary amines into diazonium salt is called diazotisation. It should be carried out below 0°c.

Solid diazonium salt acts as an explosive. Any compound which can decompose to give gaseous products spontaneously acts as an explosive.

Aromatic diazonium salts are stable at 0°c due to resonance. Hence, can be isolated.

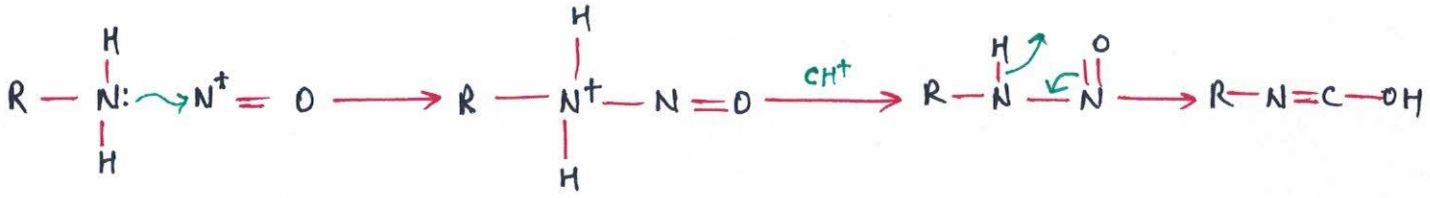
But aliphatic are unstable even at 0°c. Hence cannot be isolated.

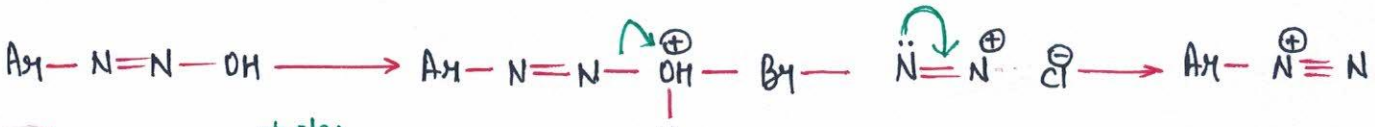
$$R-N=N^+\,Cl \longrightarrow R^+ + N_2 + Cl^- \xrightarrow{H_2O} R-OH + N_2$$

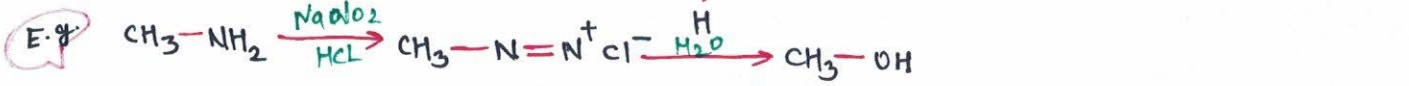
MECHANISM

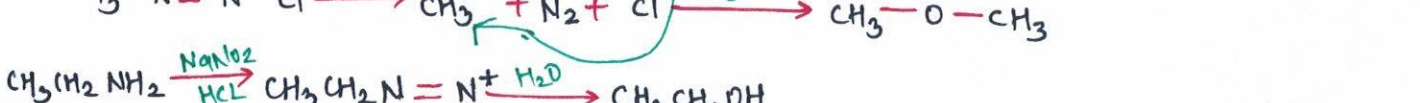
$NaNO_2$ $\quad$ HCl $\quad$ $NaCl$ $\quad$ HNO_2

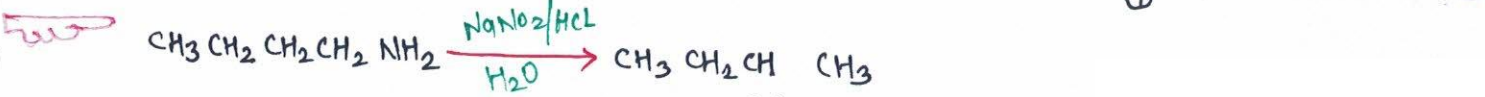
$$H-O-N=O + H^+ \longrightarrow H-\overset{\oplus}{O}(H)-N=O \longrightarrow N^+=O$$

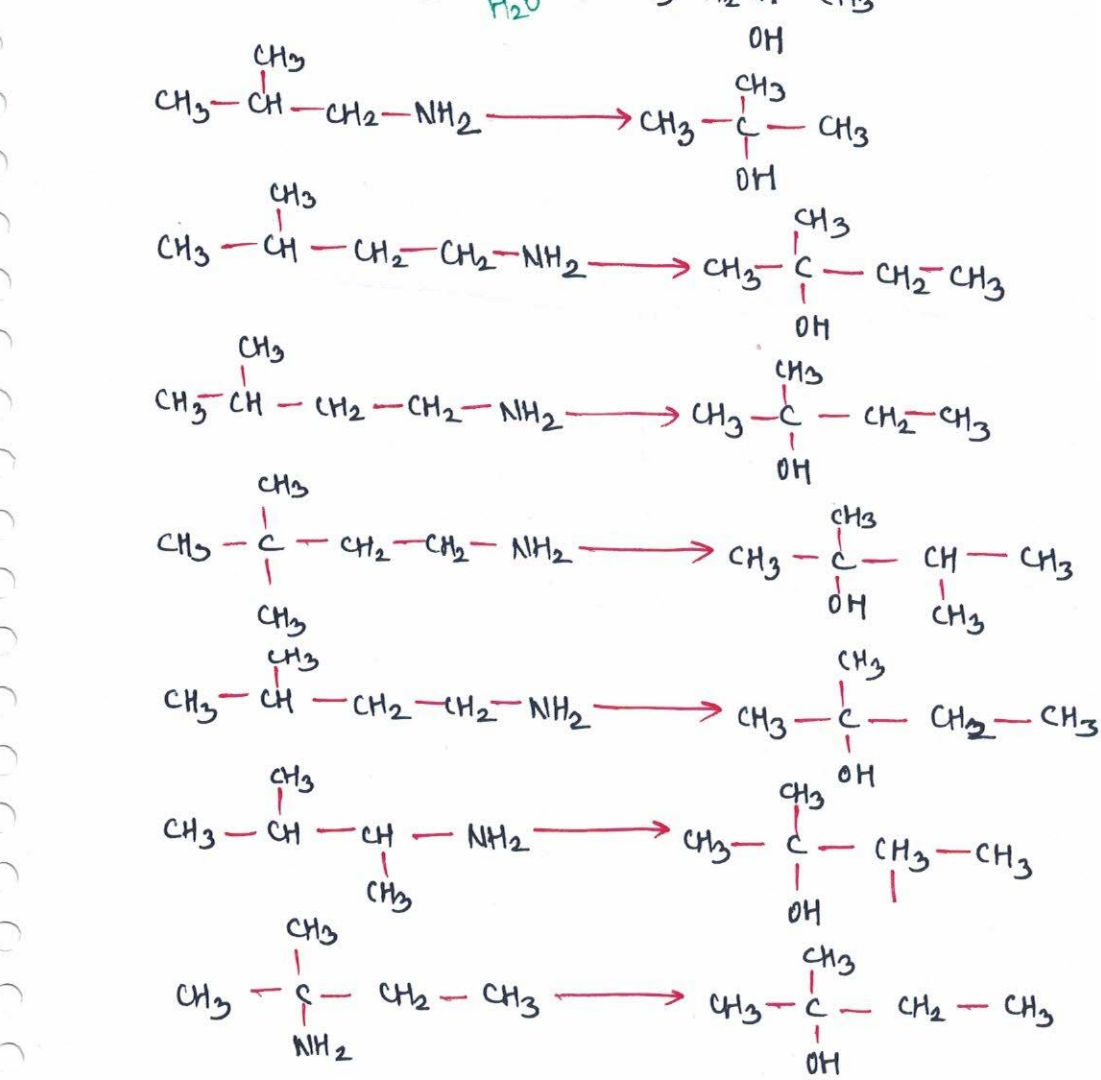


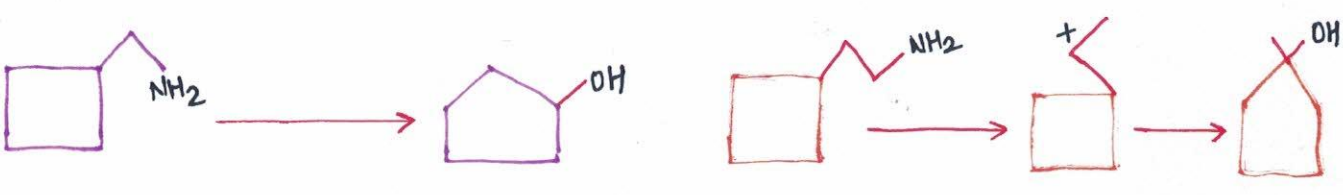


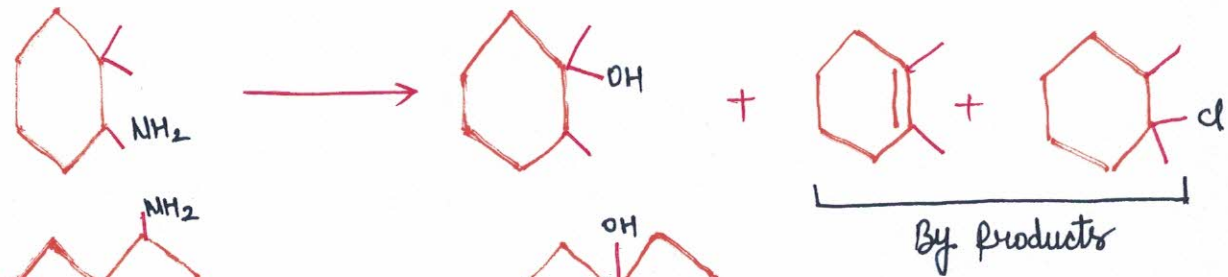


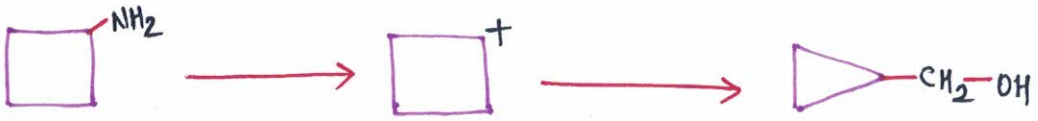


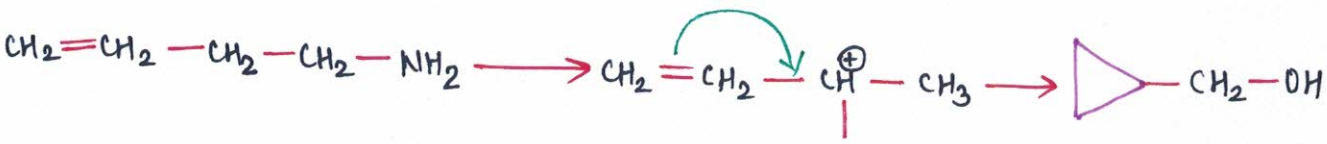


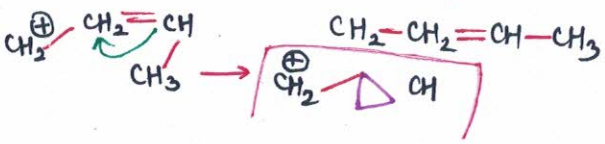


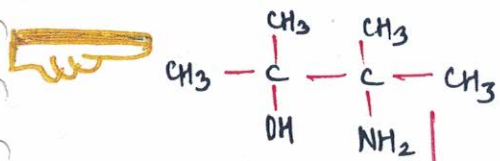


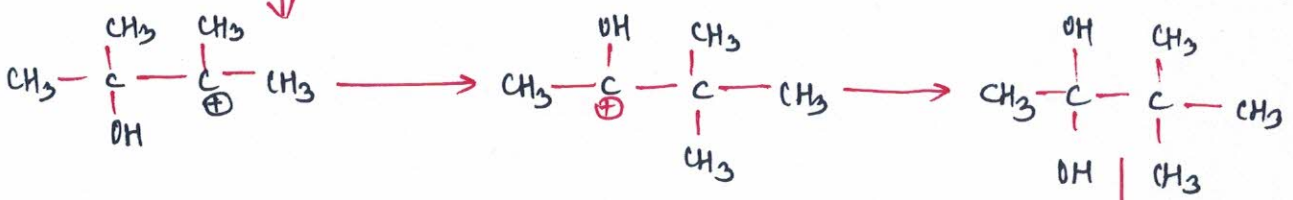


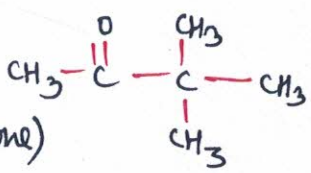






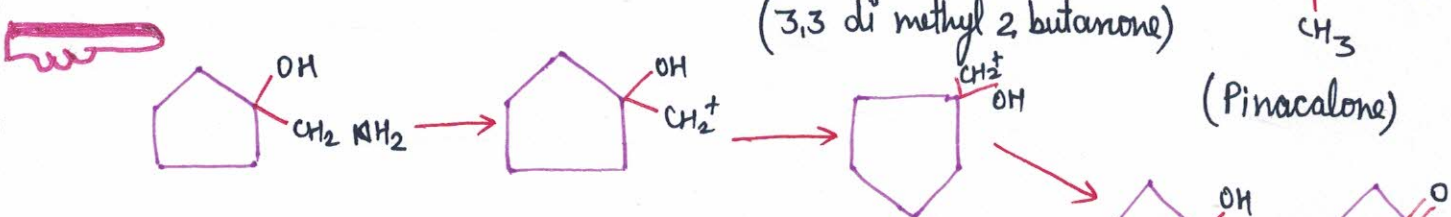


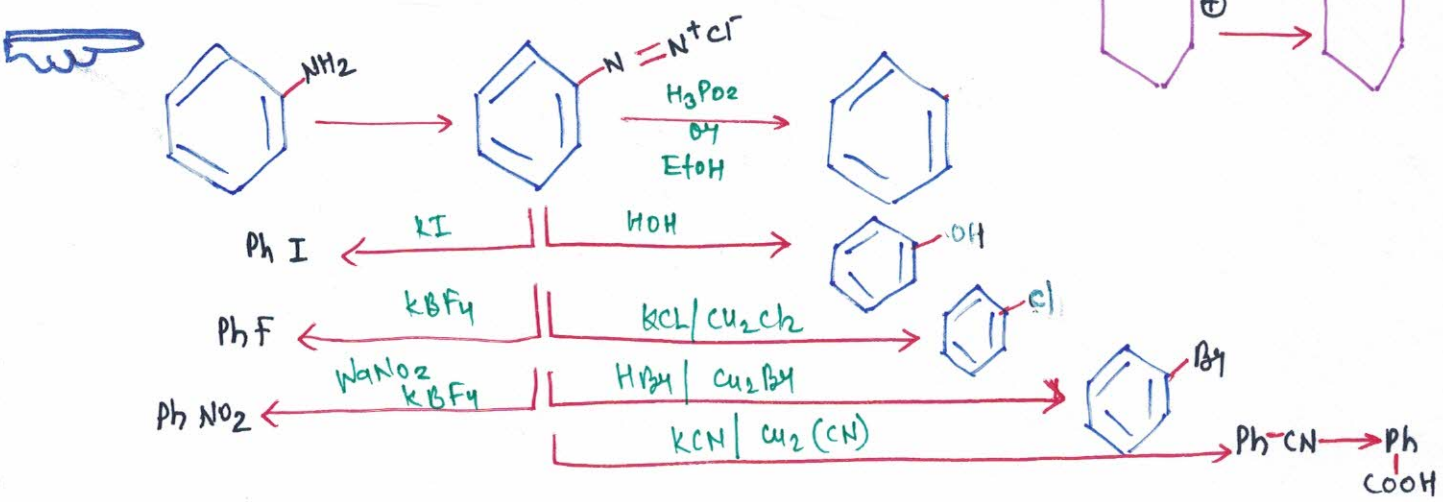




(3,3 di methyl 2 butanone)

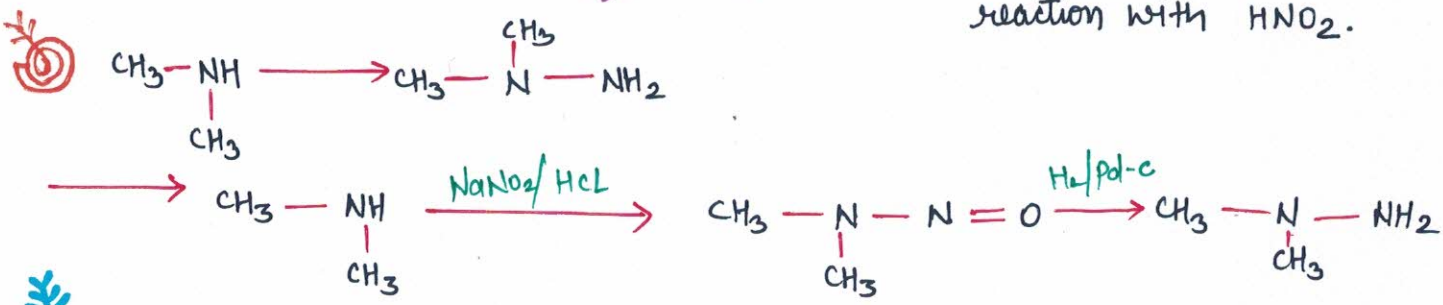
(Pinacalone)

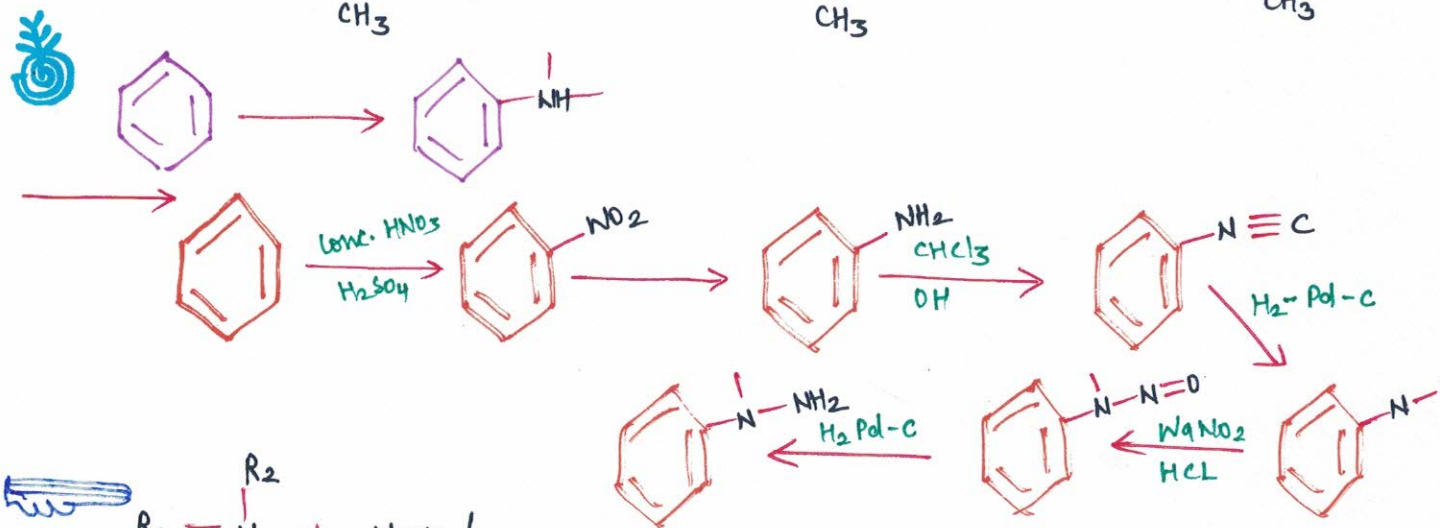


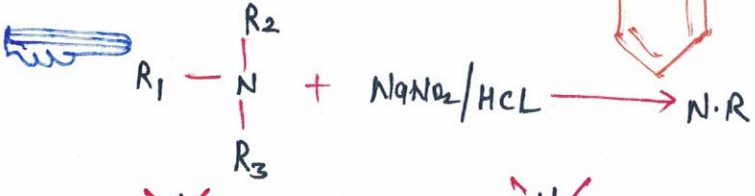


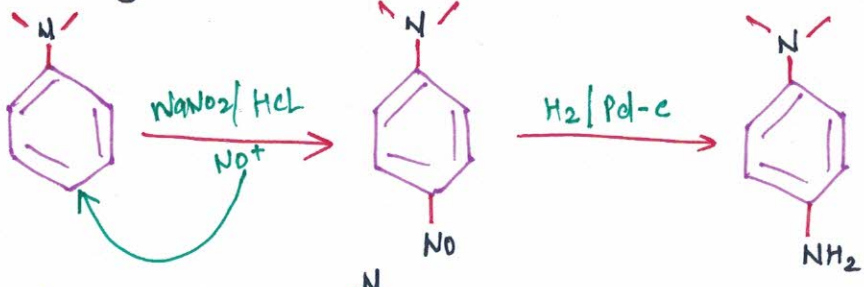
(N nitroso dimethylanine)

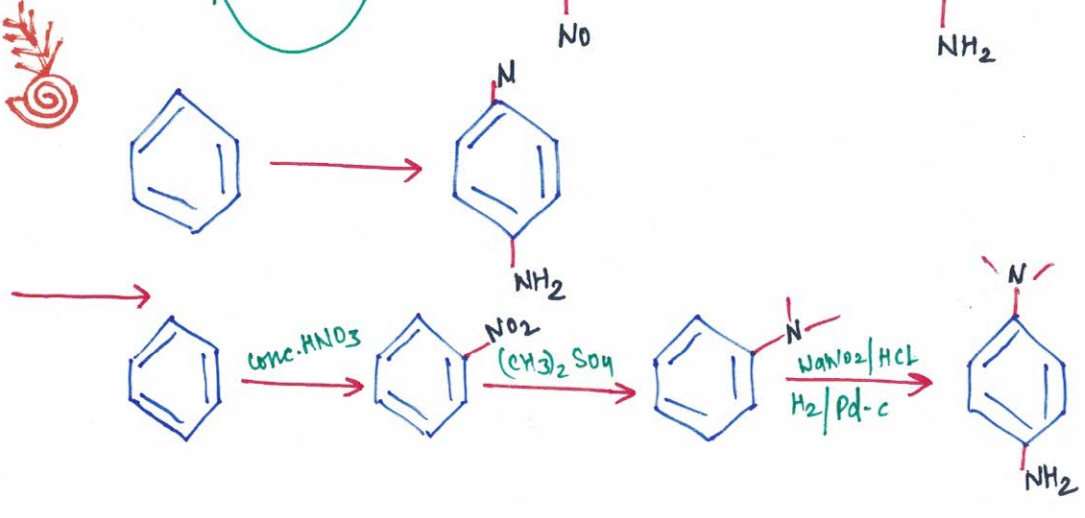
Secondary amines convert into nitro compounds on reaction with HNO_2.





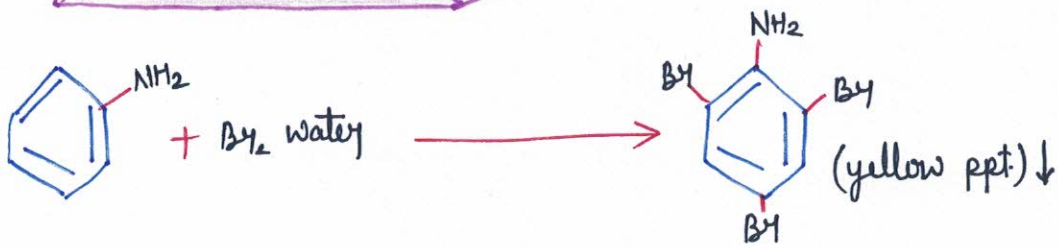


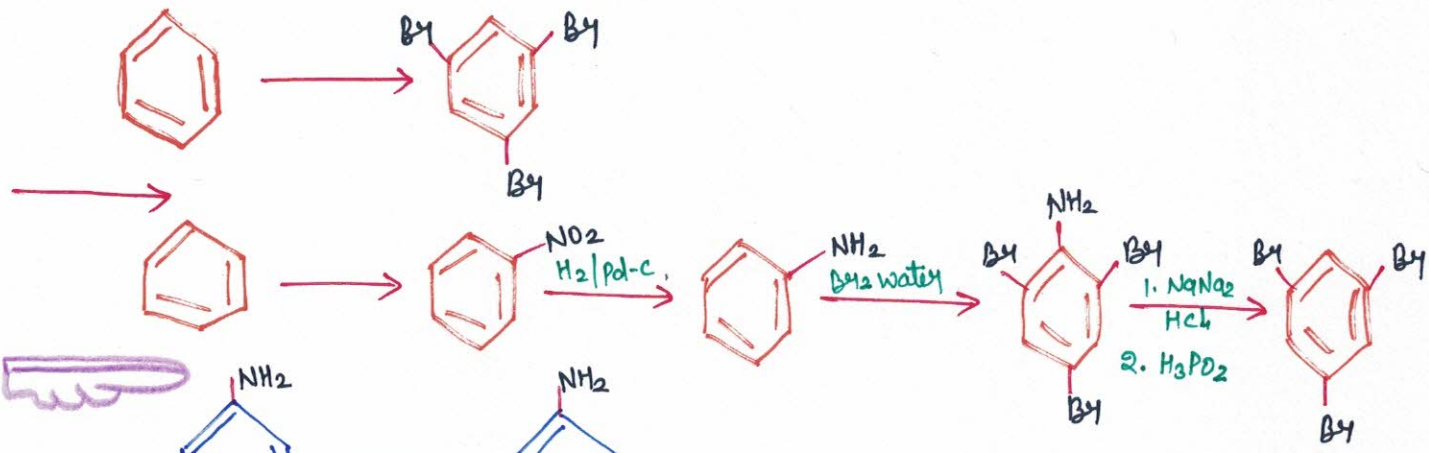


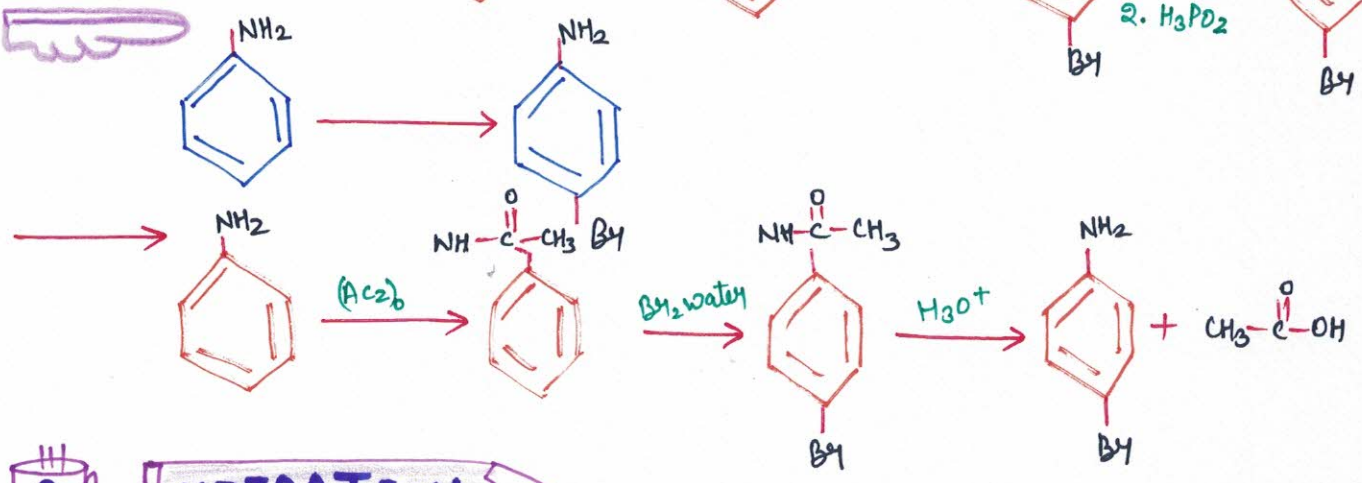


RING SUBSTITUTION REACTIONS

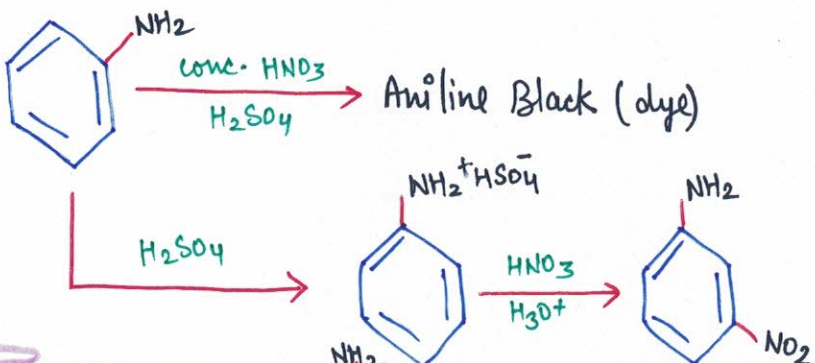
1. BROMINATION

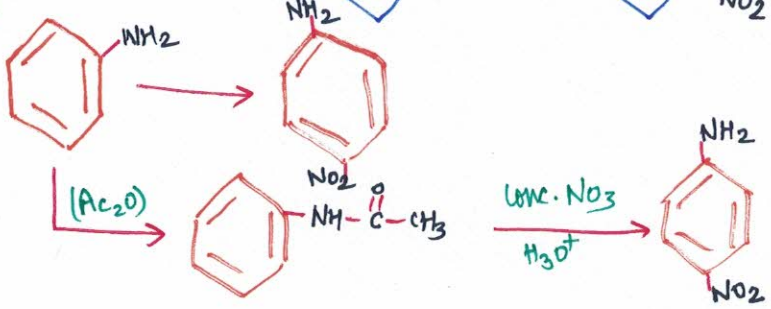


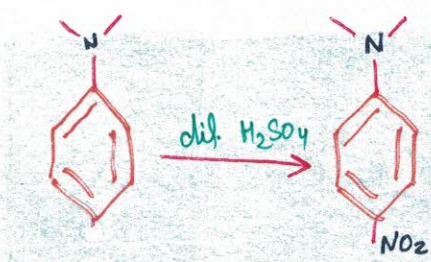




2. NITRATION

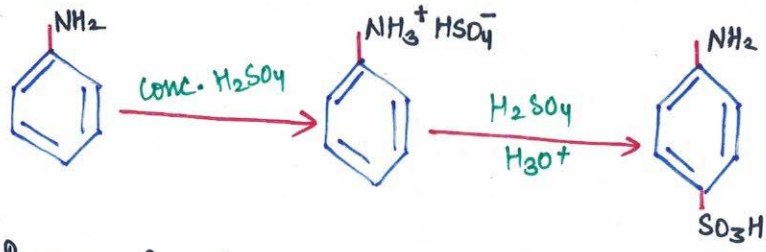






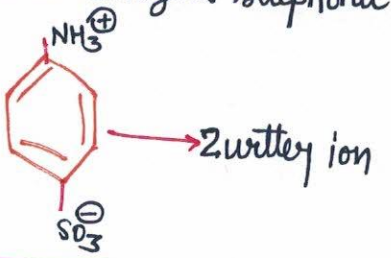
To deactivate aniline so that it does not undergo oxidation we use (Ac_2O) and then we hydrolyse.

3. SULPHONATION



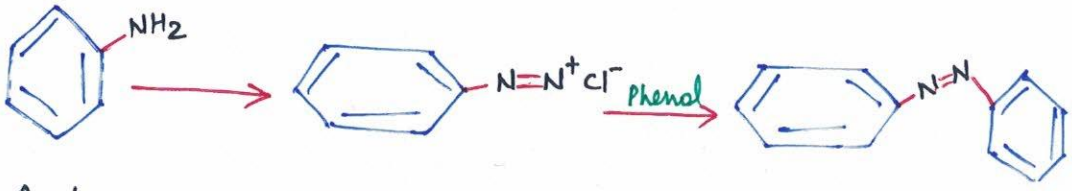
(Sulphanilic acid)

{Para amino benzene sulphonic acid → Sulphanlic acid}



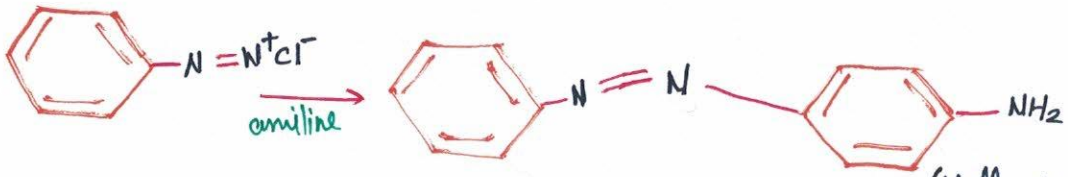
→ Zwitter ion

4. AZOCOUPLING REACTIONS

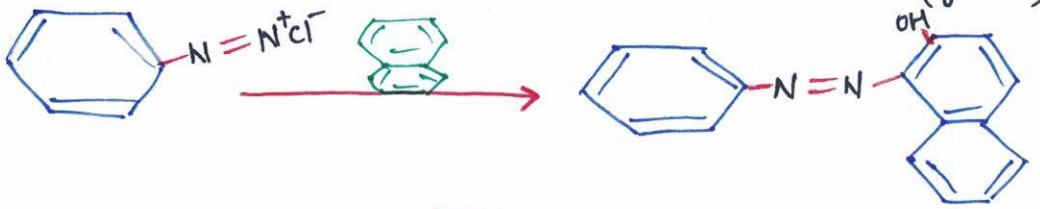


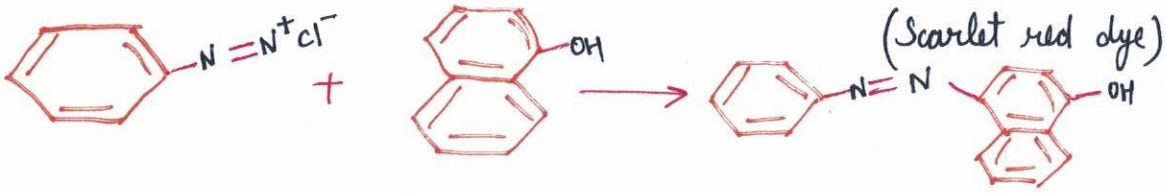
Azobenzene: 

It shows Geometrical isomerism.

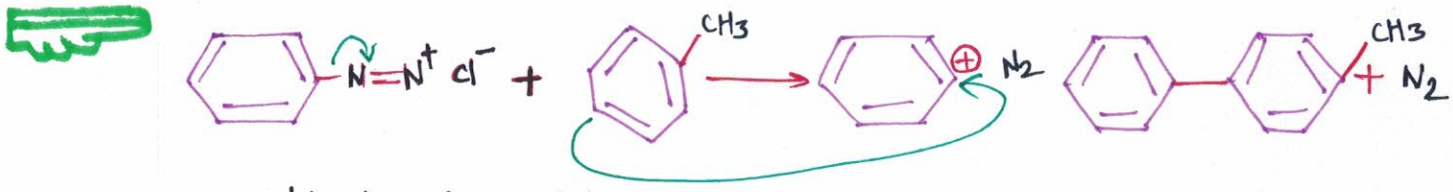


(yellow)



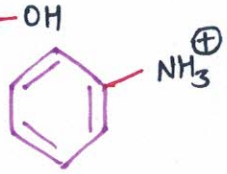


(Scarlet red dye)



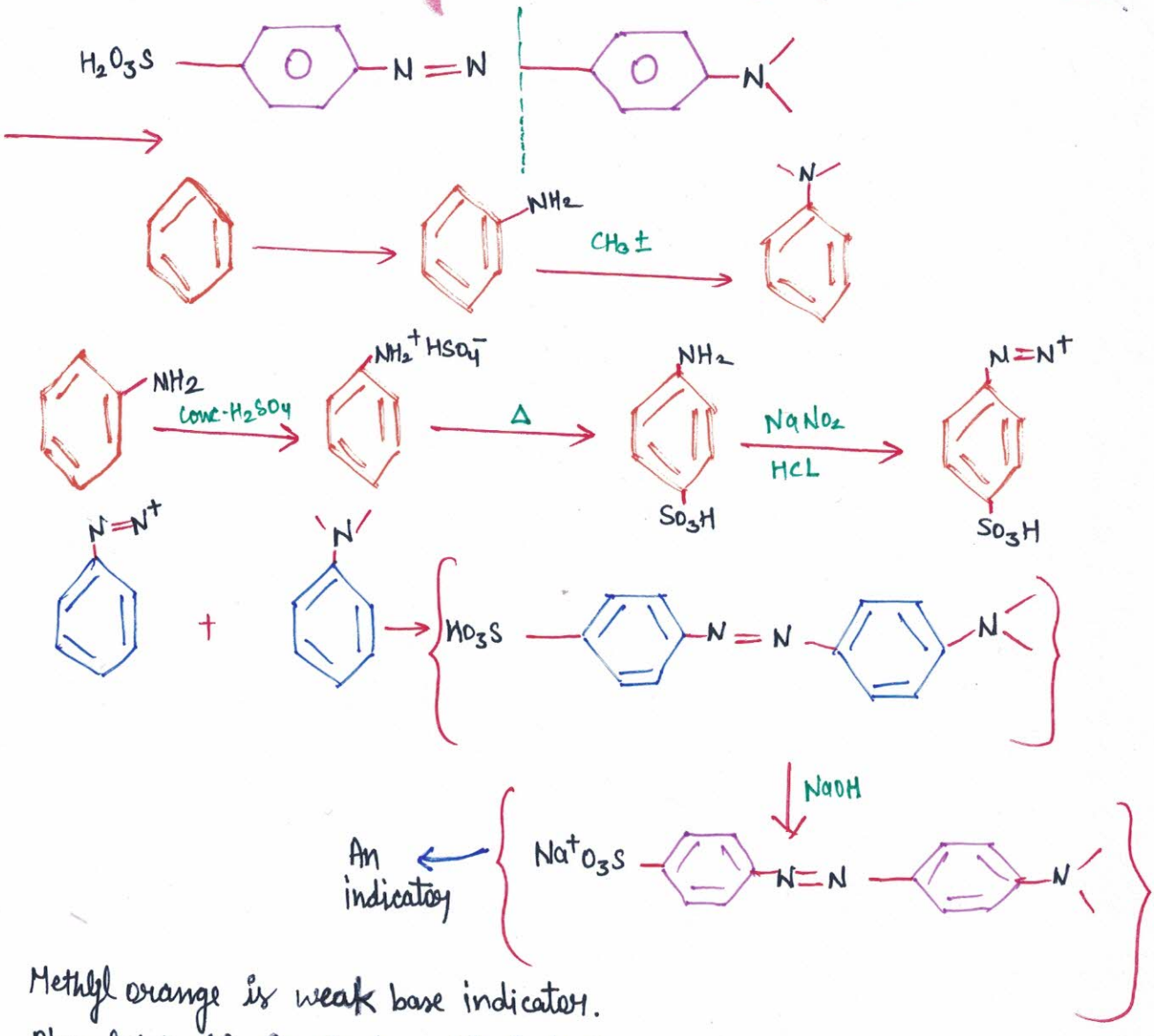
Coupling should be done in weak acid or weak base.

In strong base, diazonium salt 

In strong acid, aniline brons 

Hence, no coupling takes place.

METHYL ORANGE



Methyl orange is weak base indicator.

Phenolphthalin is weak acid indicator.

Both of them are less reactive than reactants so they react at equibalence point in the end.

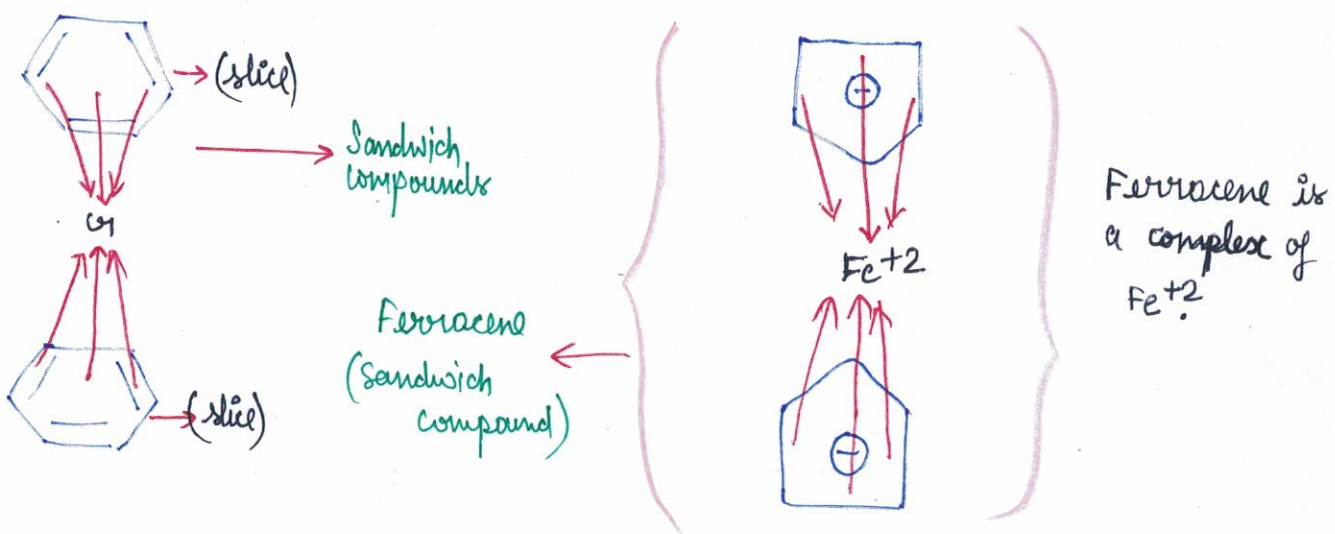
AROMATIC COMPOUNDS

PROPERTIES

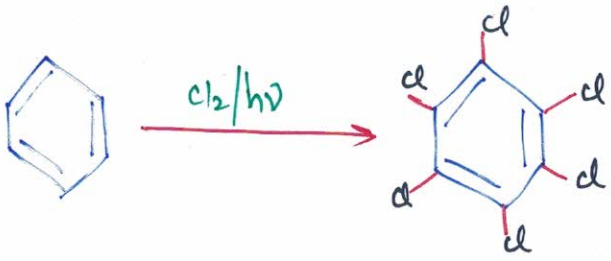
1. Electrophilic substitution
2. Reduction
3. Oxidation
4. Radical Addition
5. π- complex formation

π COMPLEX FORMATION

Benzene is a tridentate due to presence of three lone pairs.



Radical Addition



(1,2,3,4,5,6 hence chloro... cyclohexane)

$(C_6H_6Cl_6)$ → Benzene hexa chloride (B.H.C)

It is also called Gammasin. used as insecticide.

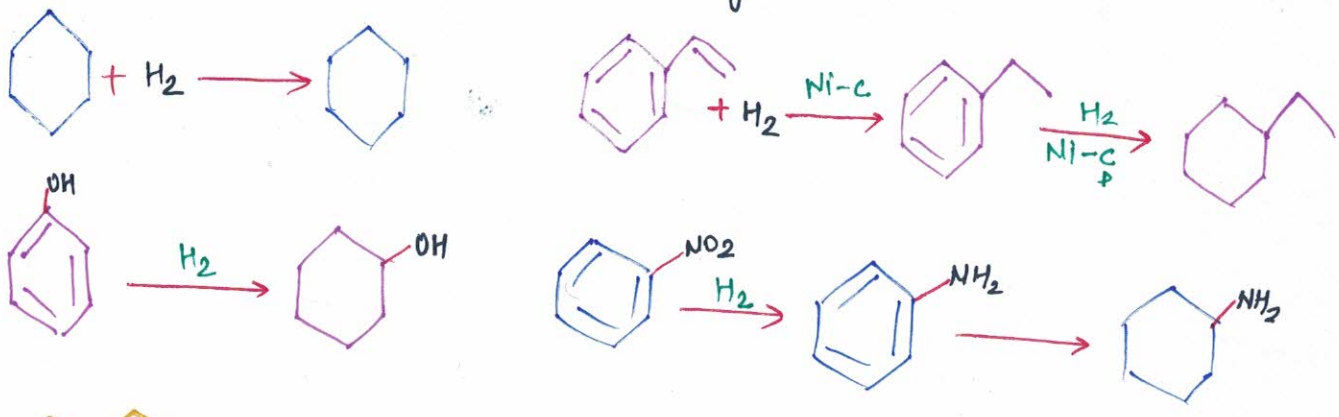
Hence chloro benzene → C_6Cl_6 → substitution reaction.

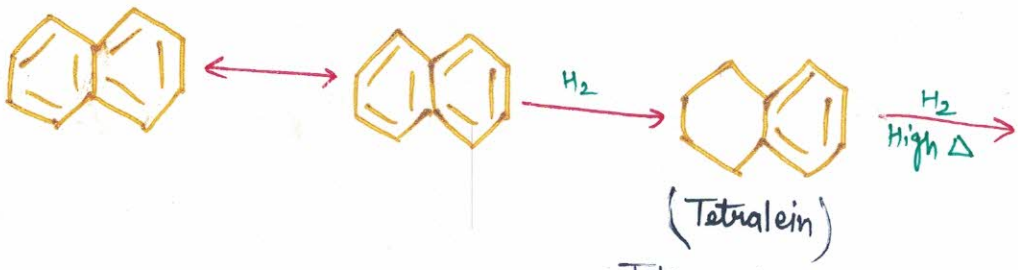
Benzene Hexa chloride → $C_6H_6Cl_6$ → radical addition reaction

Reduction

$CH_2=CH_2 \longrightarrow CH_3-CH_3$ (Sebastion senderenes Reaction)

Reduction of benzene is not as easy as that of an alkene due to aromatic nature. Hence energy of activation of benzene is higher.

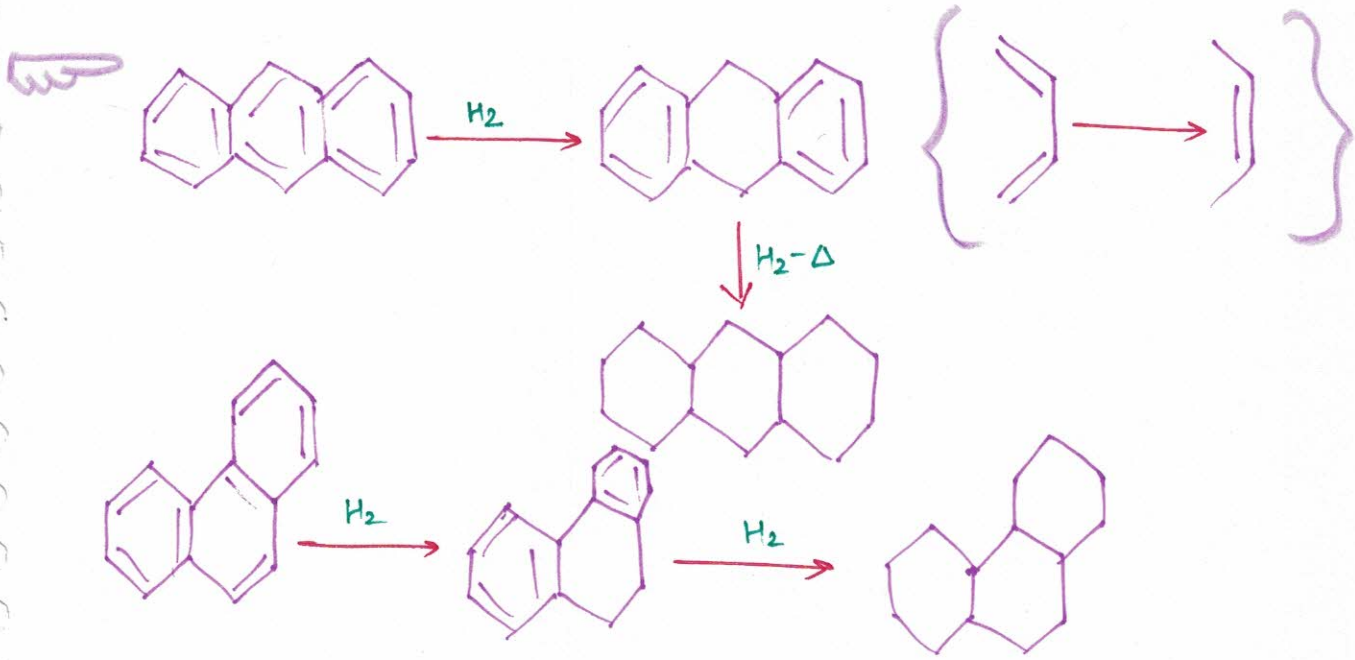




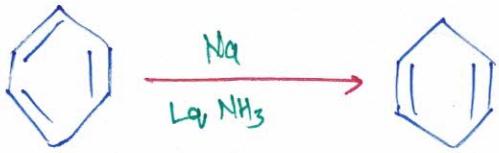
(Tetralein)
Tetra Hydro Napthalene

(Decalein)
Deca Hydro Napthalene

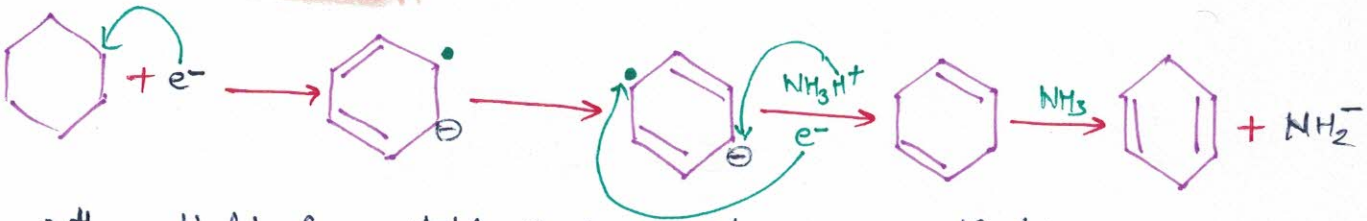
Activation energy of benzene in 36 but A.E of napthalene is not 36×2 = 72 but only 50 because only one ring is benzanoid.



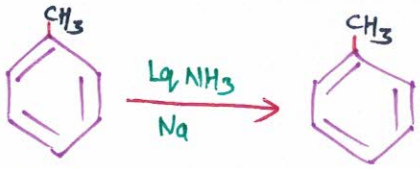
Birch Reduction

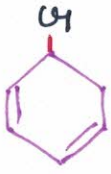


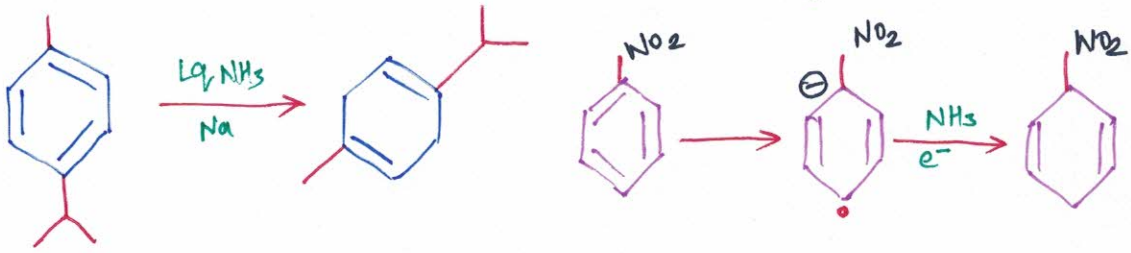
MECHANISM



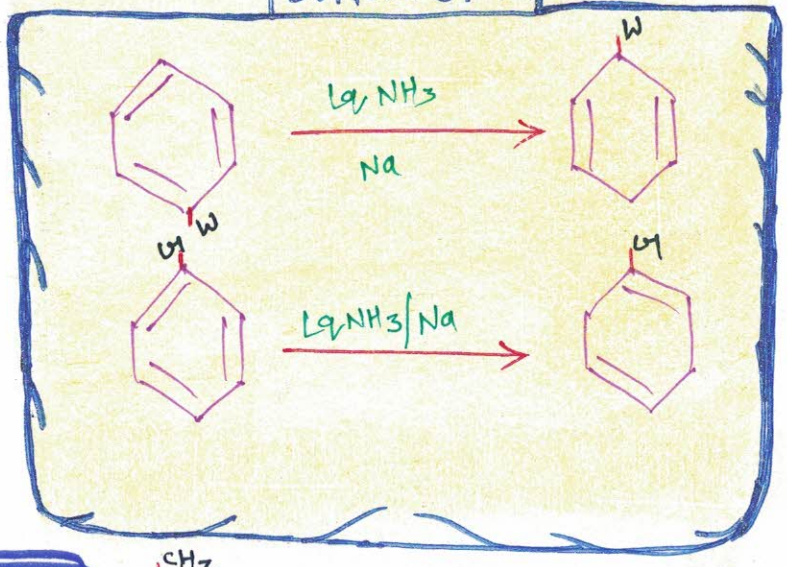
ortho radical ion is unstable it changes to para radical ion.

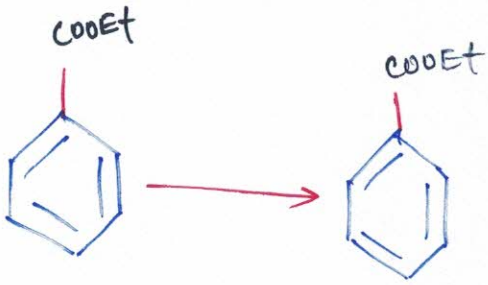


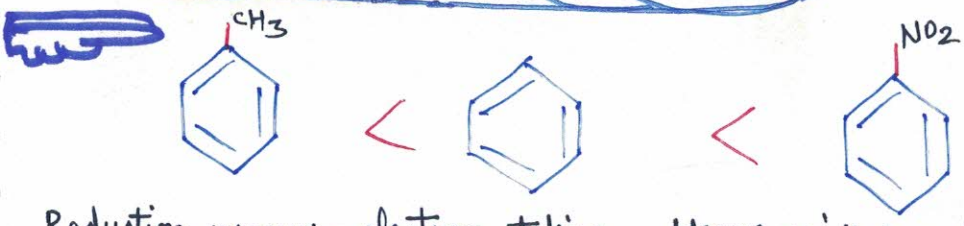
If releasing group,  is formed,  is not formed in birch reduction



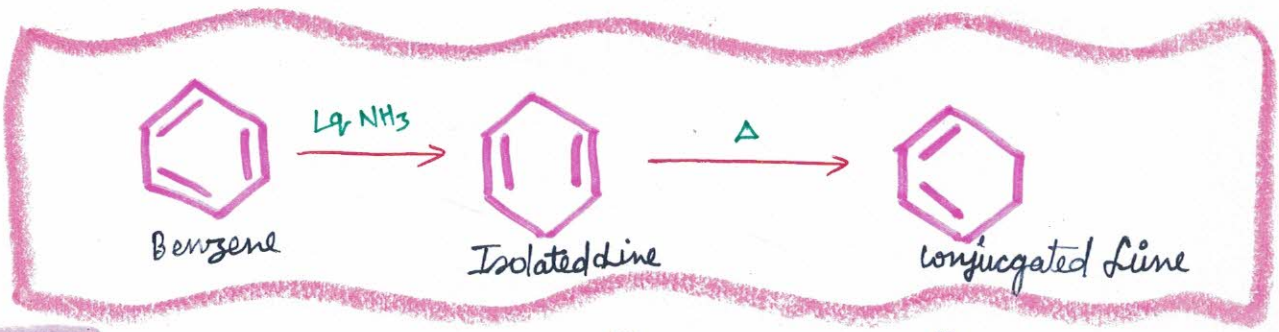
CONCLUSION

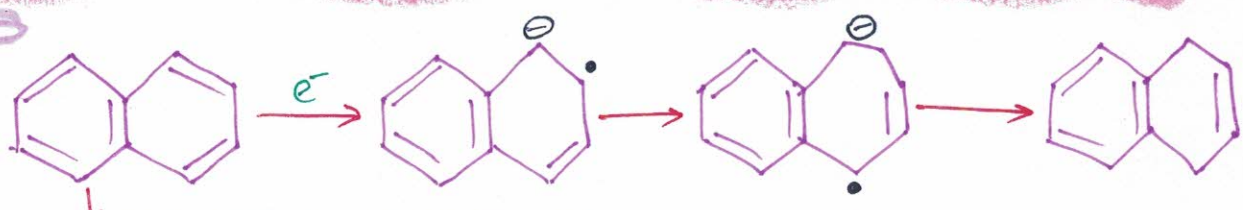




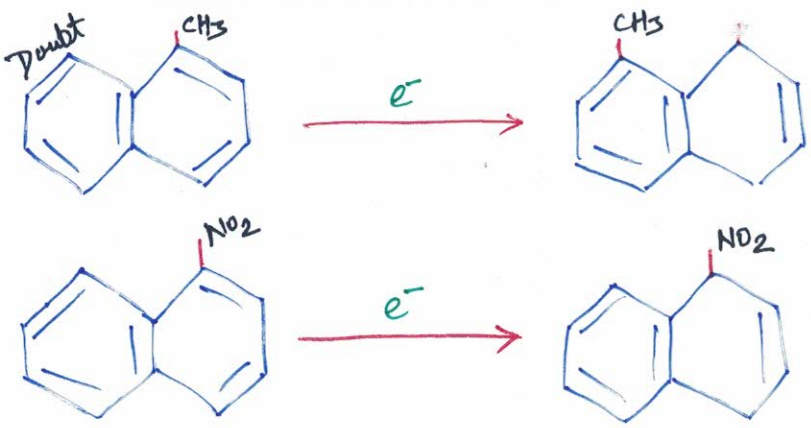


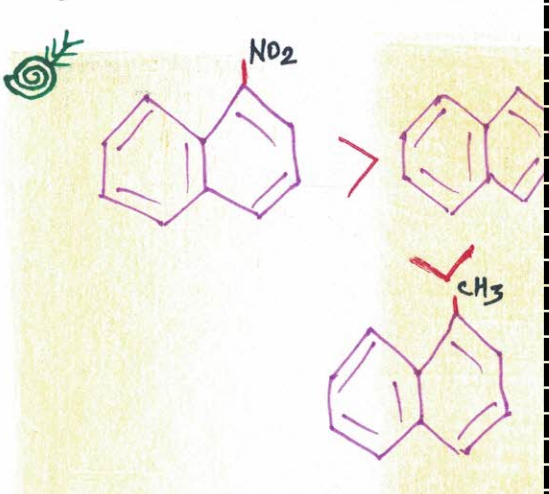
Reduction means electron taking. Hence withdrawing groups attached to benzene can be reduced more easily.



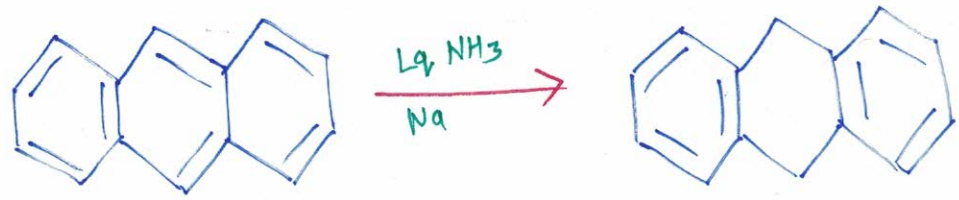


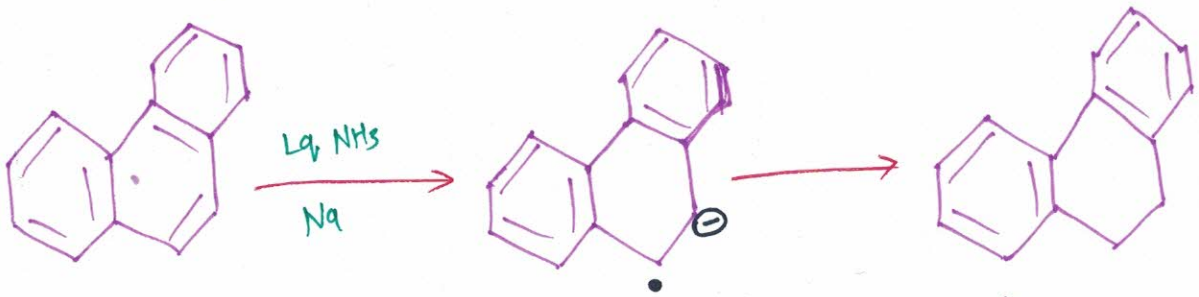
It is stable due to resonance.





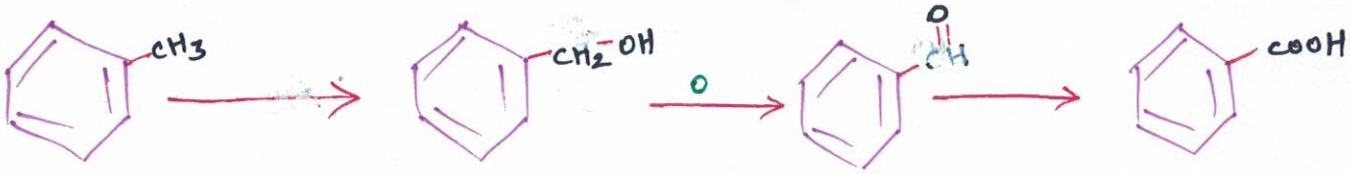
Rate of reduction

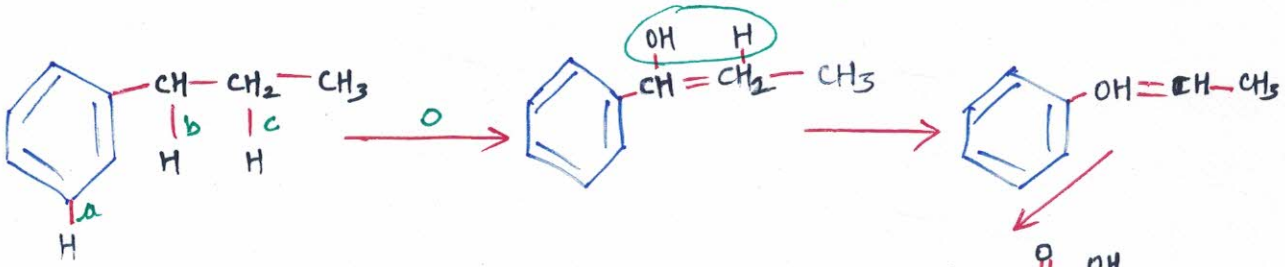




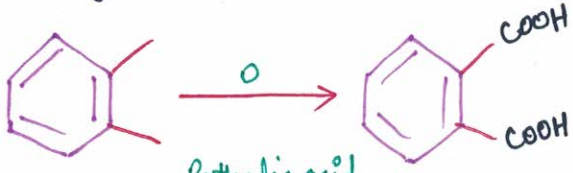
(Here ortho radical is formed).

Oxidation:

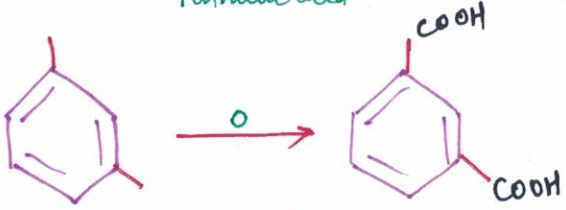




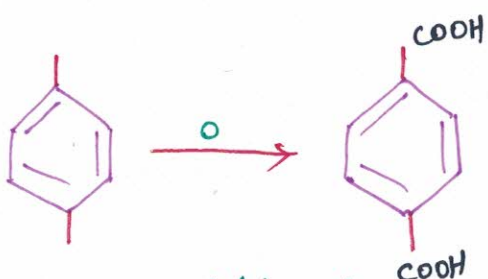
"b" is longest bond. Hence weak bond. so, it undergoes oxidation.



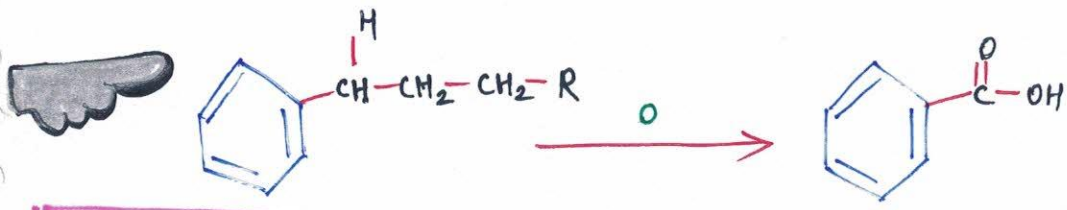
Pathalic acid



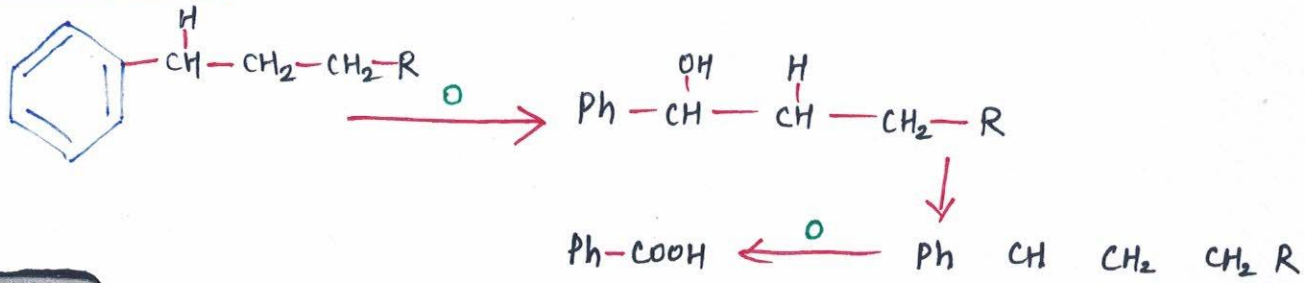
Isophtalic acid

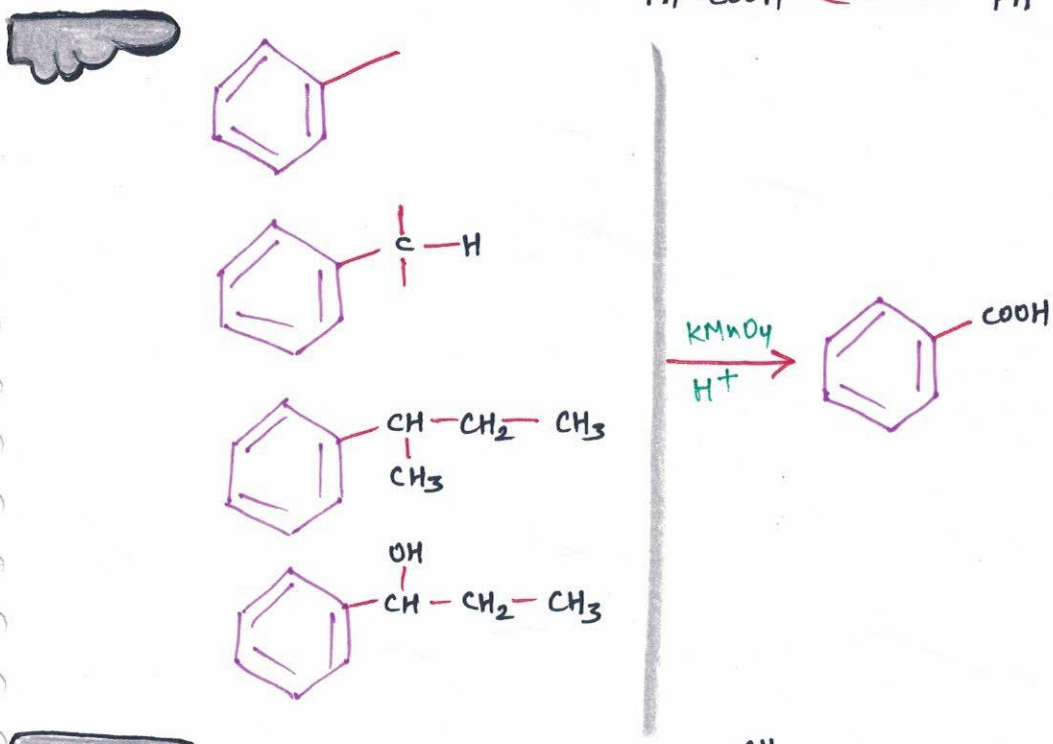


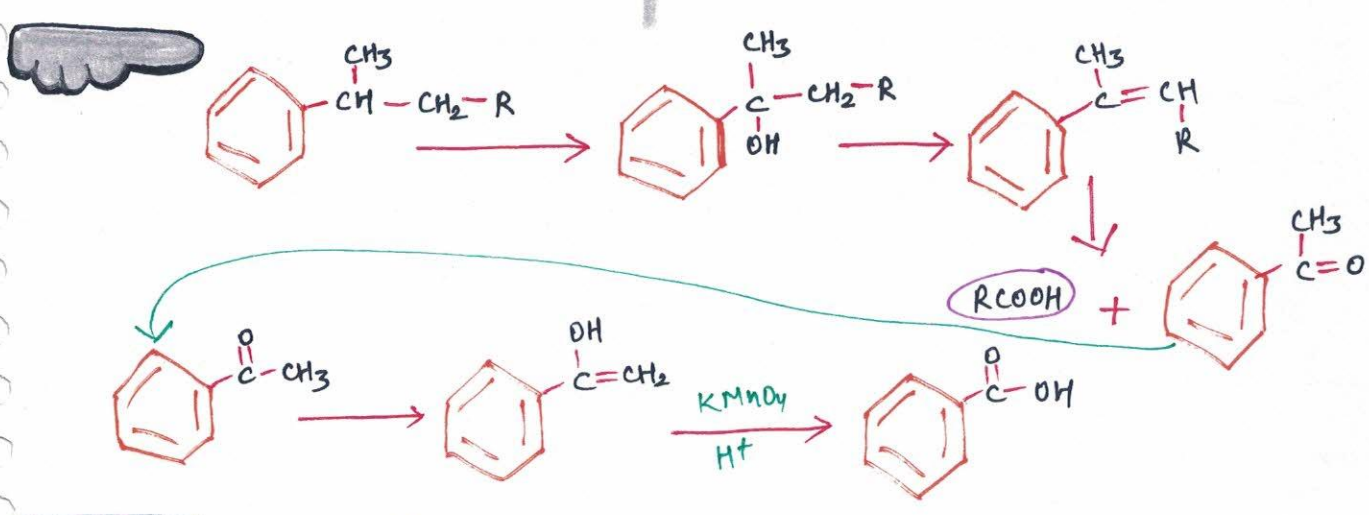
Terphtalic acid

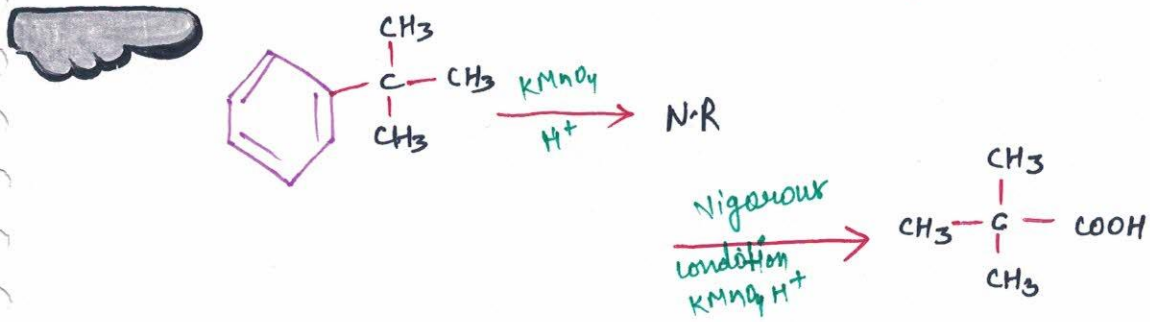


MECHANISM

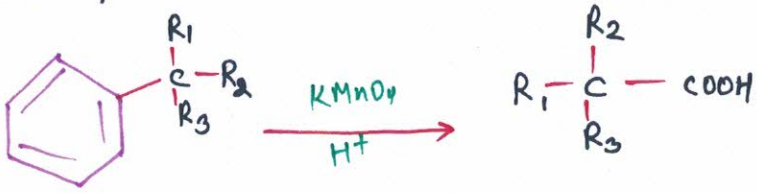


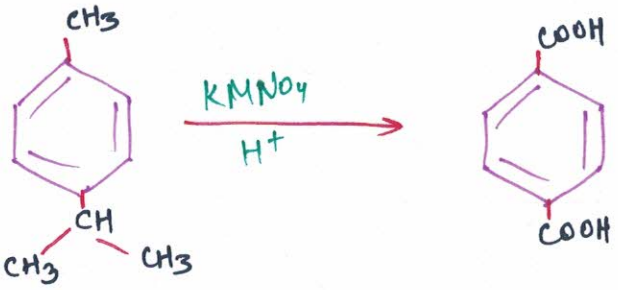


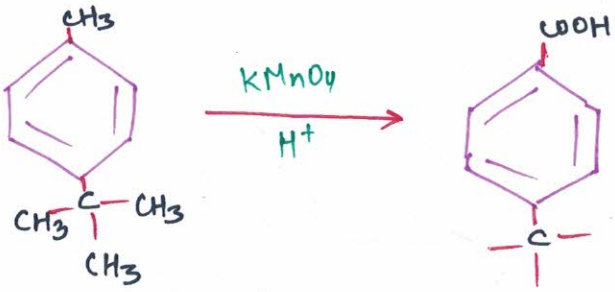


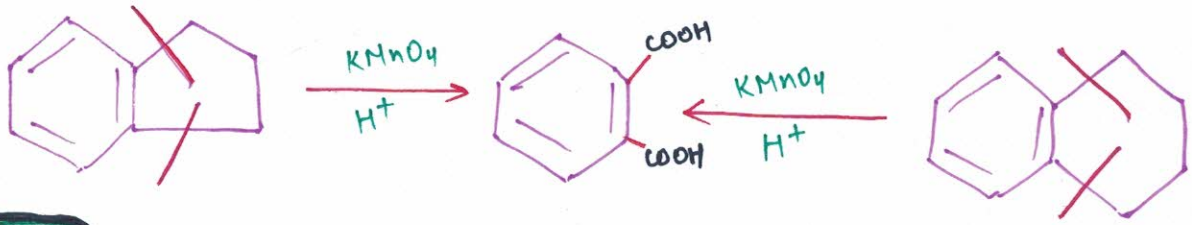


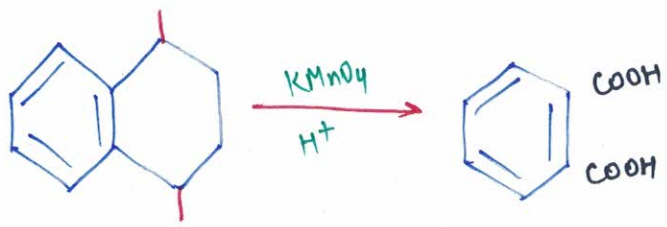
IMP.... If there is no β hydrogen in side chain, then ring undergoes oxidation.

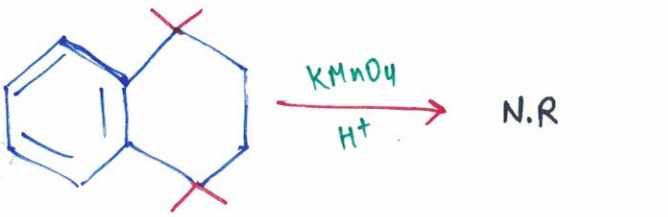












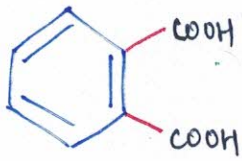
No presence of β hydrogen in last case.

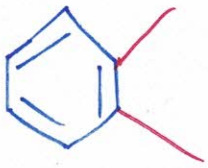
Question

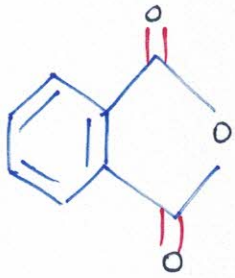
Soln

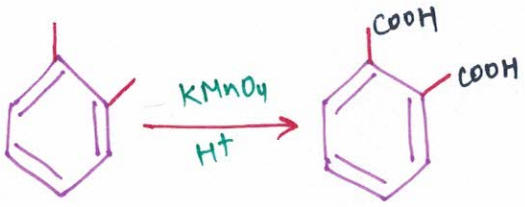
(A) (C_6H_{10}) $\xrightarrow{KMnO_4}$ (B) $(C_8H_6O_4)$ $\xrightarrow{\Delta}$ (C) $(C_8H_4O_3)$

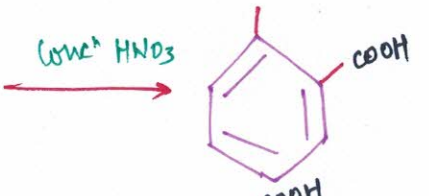
$C_8H_{10} \rightarrow \frac{18-10}{2} = \frac{8}{2} = 4$

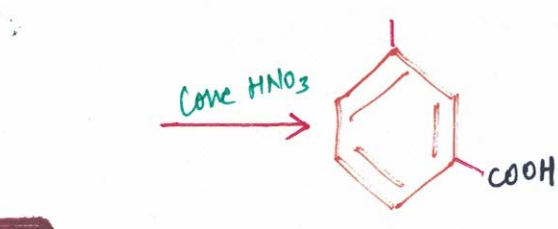
B ⇒ 

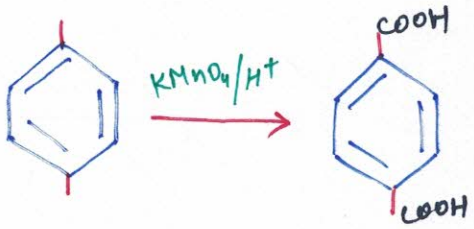
A. 

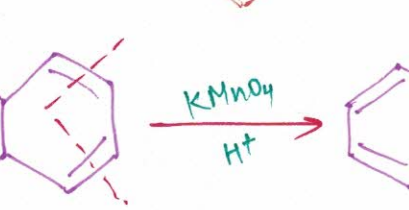
C. 

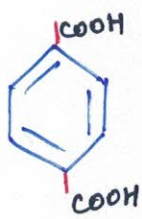




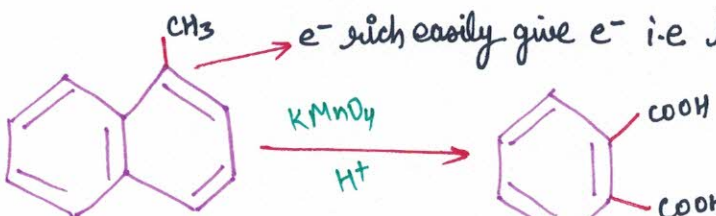








(2)

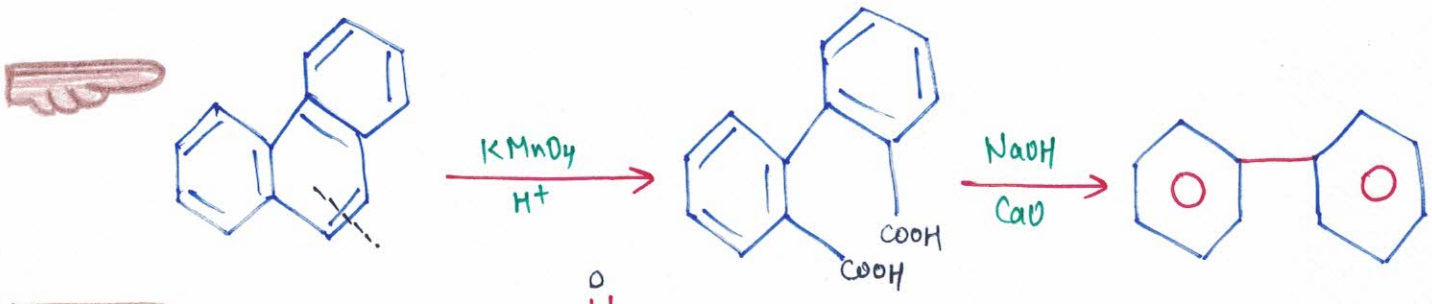


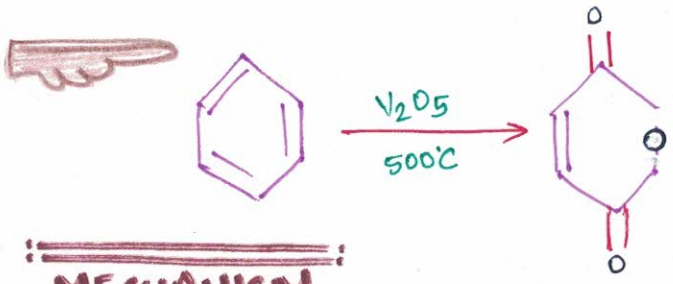
e^- rich easily give e^- i.e it can be oxidised easily.

(1)

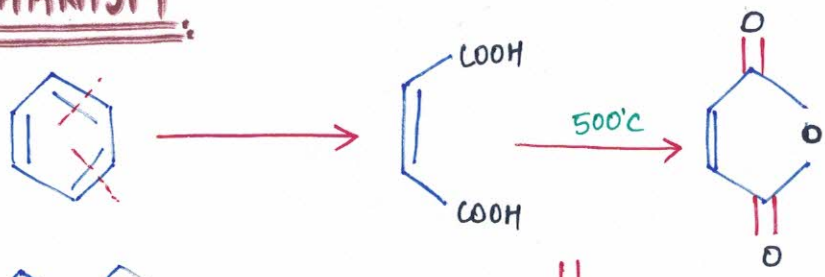
(3)

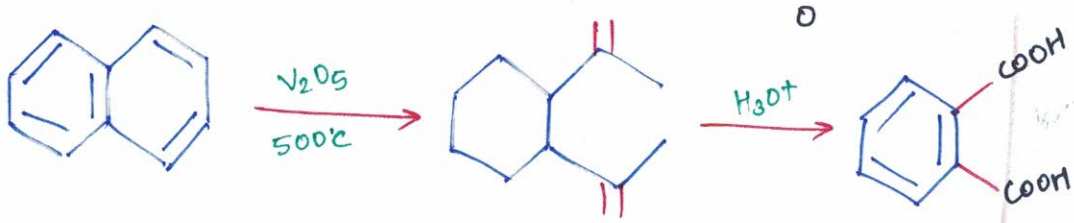
RATE OF OXIDATION

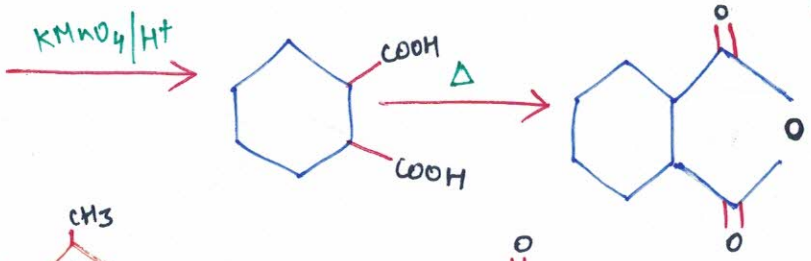




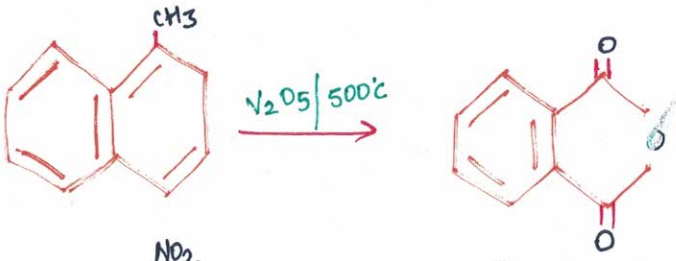
MECHANISM

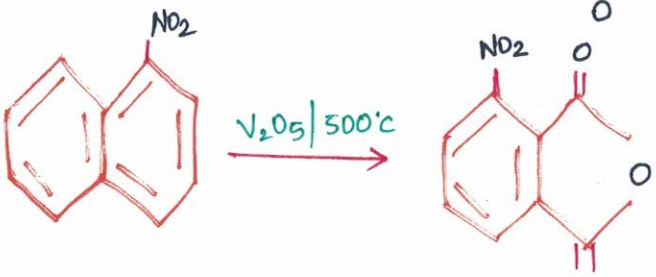






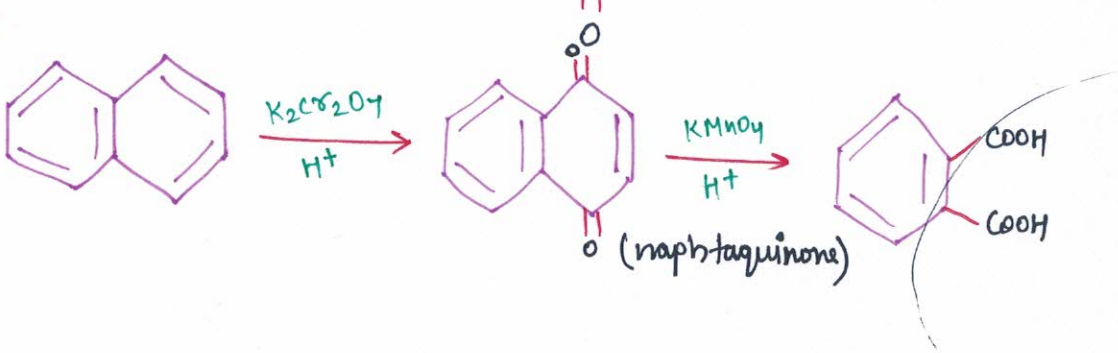
Pthalic anhydride



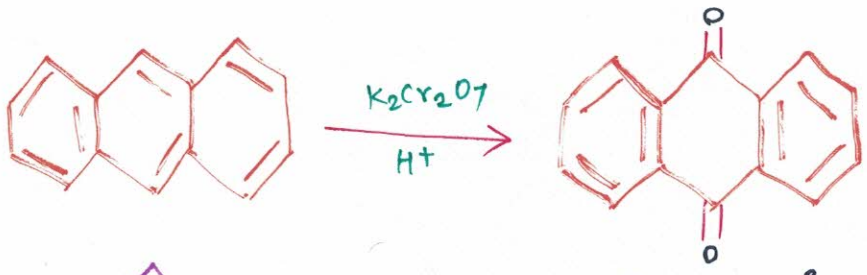


$V_2O_5 \rightarrow$ anhydride

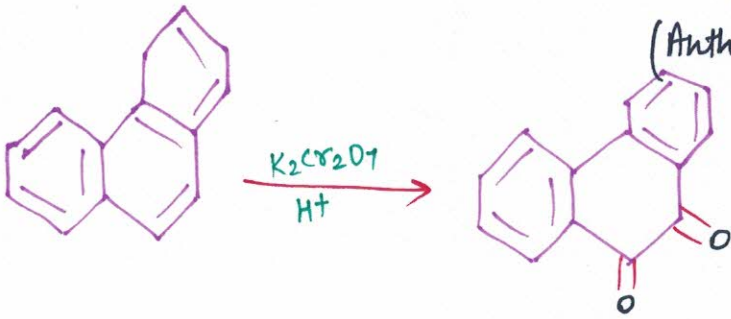
$KMnO_4 \rightarrow$ acid



(naphtaquinone)



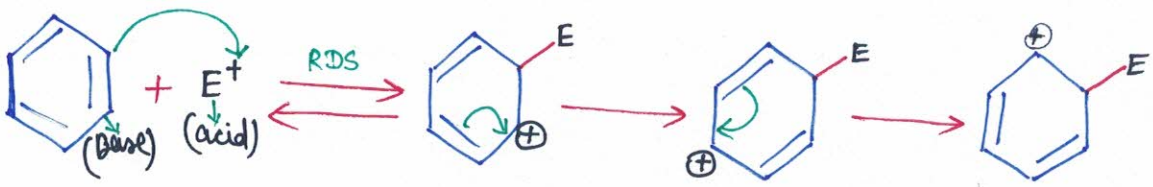
(Anthraquinone)

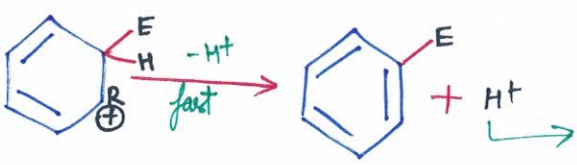


(Phenanthraquinone)

Electrophilic substitution

Benzene is a nucleophilic as it has 3 lone pairs.



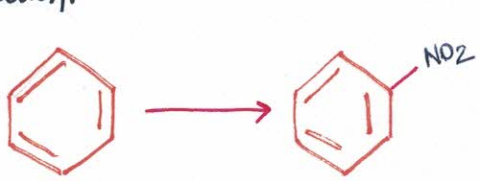


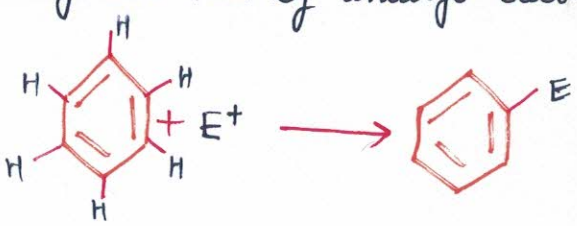
→ leaving group (electrofungal)

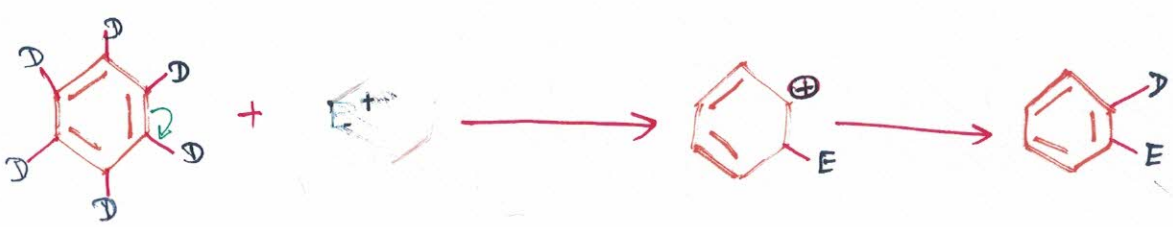
Aromatic compounds undergo electrophilic substitution.

Electrophilic substitution reaction can be regarded as acid base reaction.

Forming benzene i.e... releasing 36 Kcl energy and undergoing electrophilic substitution is more preferable than forming 28.6 Kcal by undergo electrophilic addition.





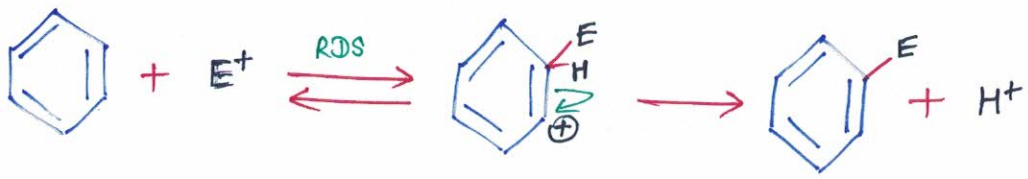


Electrophilic substitution do not show β hydrogen isotopic effect as the carbocation is not formed by removal of H^+. Hence rate of reaction is same.

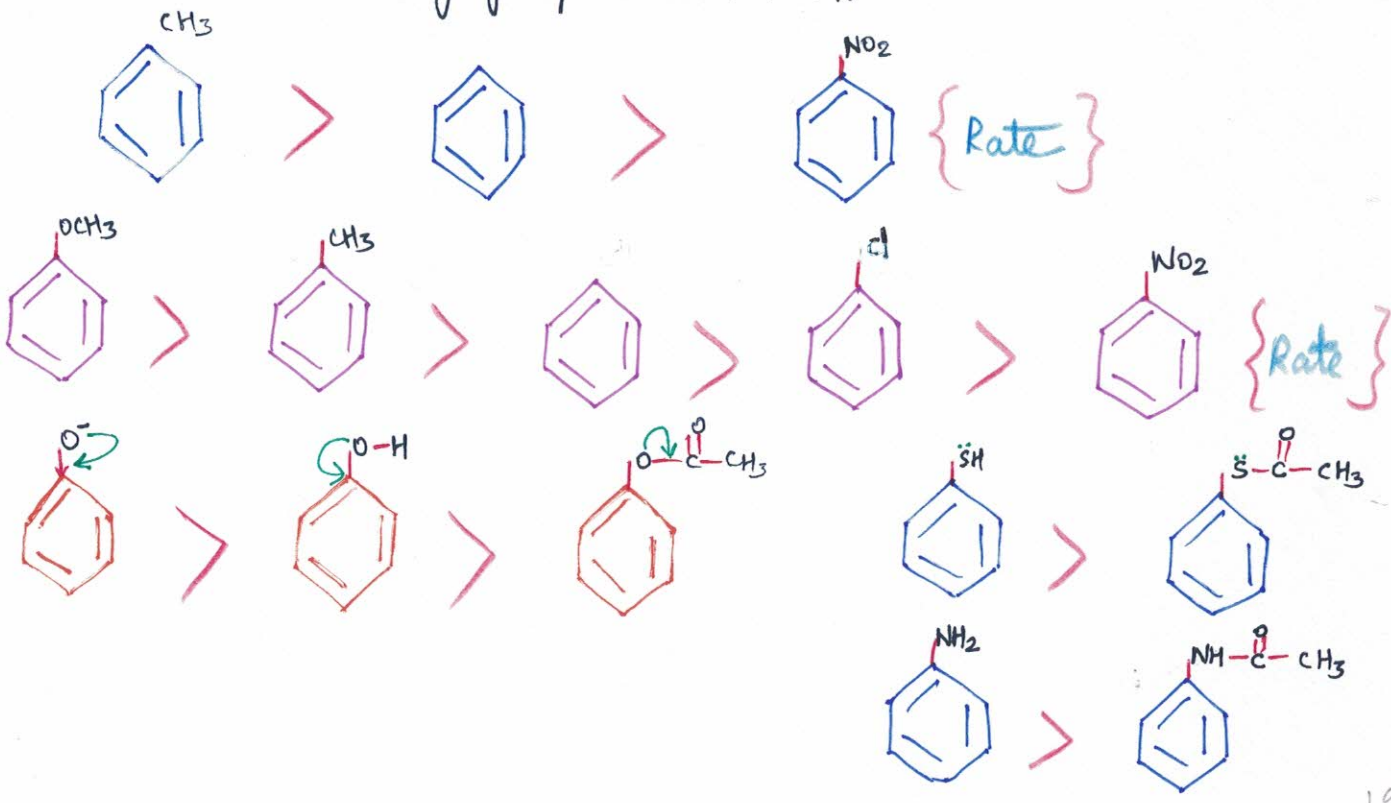
This statement is true for all electrophilic substitution reactions which are irreversible. It is not true for reversible reactions.

If electrophilic reactions is irreversible it will not show β hydrogen isotopic effect. But if it is reversible, it will show β hydrogen isotopic effect.

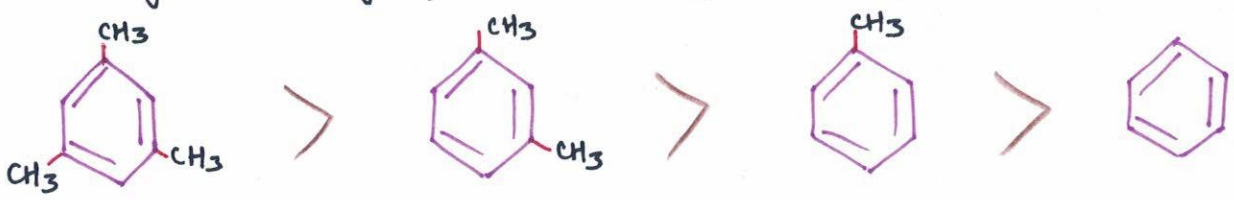
Electrophilic Substitution & Rate

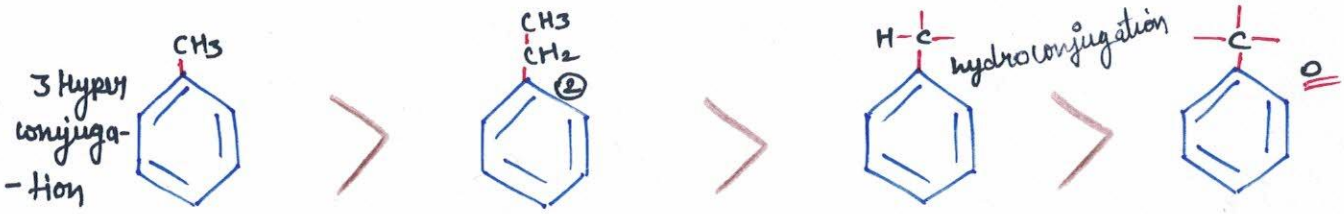


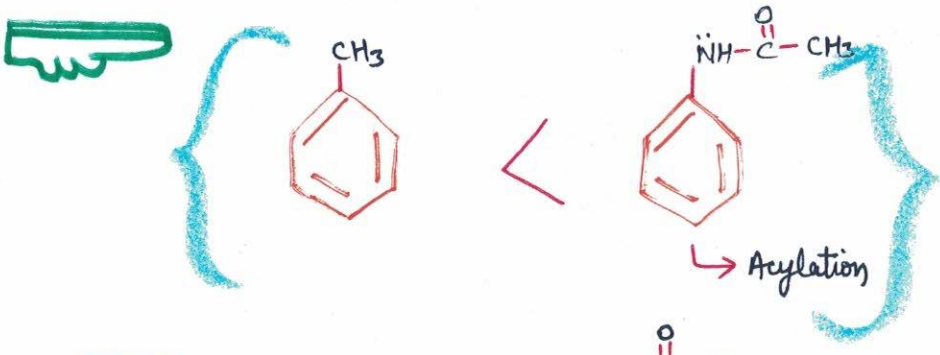
All releasing groups increase the rate of electrophilic substitution as their releasing nature increases e⁻ density in ring & stabilise the intermedia carbocation formed. But if a withdrawing group is attached donating tendency decreases, basic nature ↓ & destabilises the intermediate carbocation formed. All withdrawing groups deactivate aromatic hydrocarbons towards electrophilic substitution and releasing groups activate them.

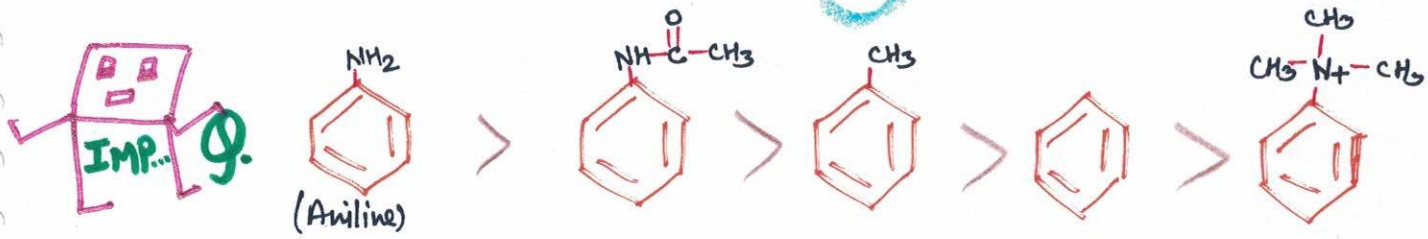


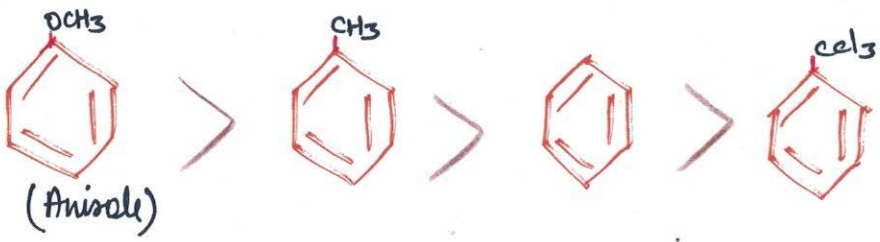
introducing $-\overset{O}{\overset{\|}{C}}-CH_3$ group is called acylation. Acylation decreases +M effect.

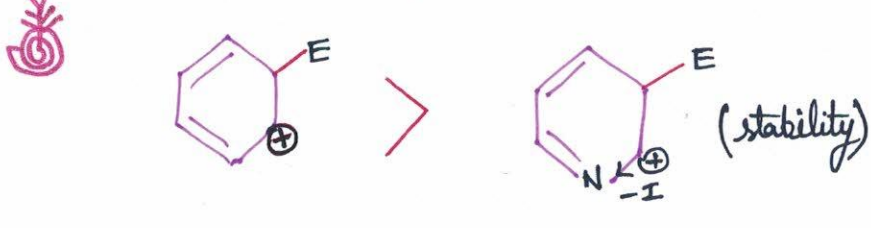


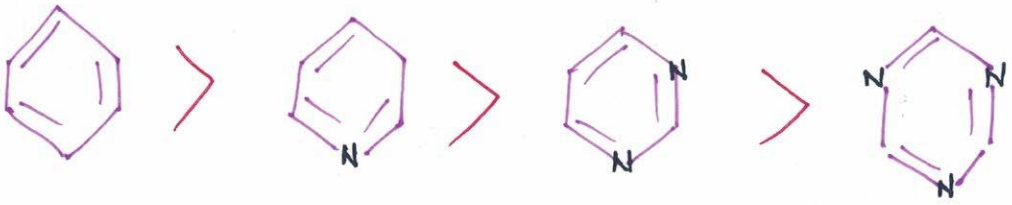


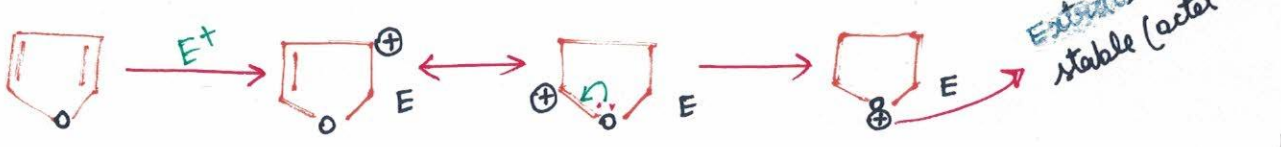




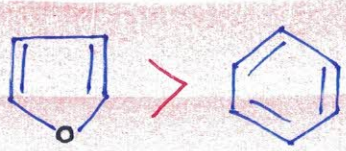


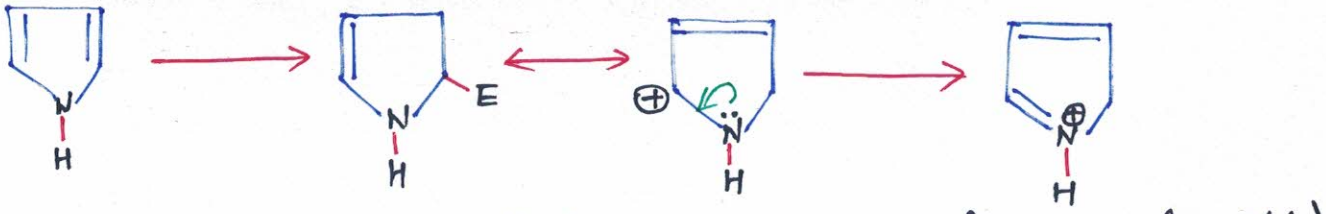






Rate of Electrophilic substitution

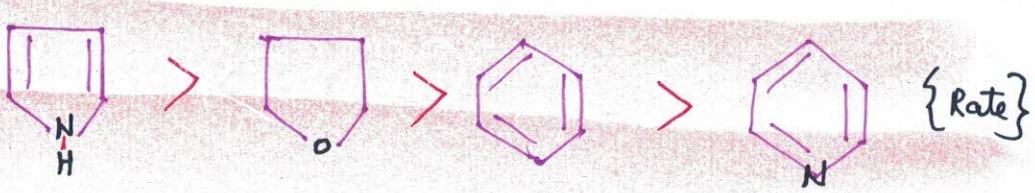




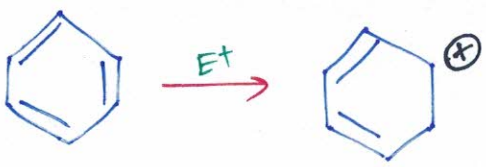
$N^+ > O^+$ (stability)

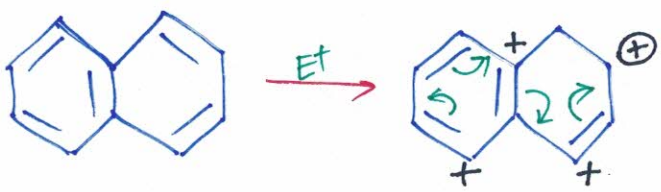
(Phenomenaly stable)

So, pyrole has a greater tendency to donate e^-.

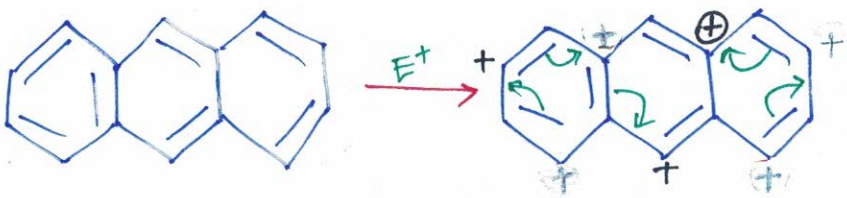


{Rate}





more delocalised

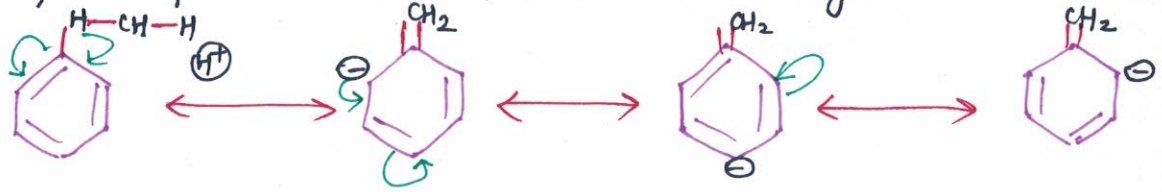


even more delocalised

{Anthracene > Naphthalene > Benzene} Rate of Reactions

If due to a group's influence, incoming electrophile goes to ortho or para, the group is ortho para directive group. And if it goes to meta position, the group is called meta directive group.

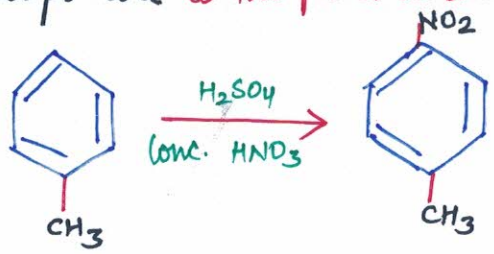
Thus, electrophilic substitution reactions are regioselective reactions.



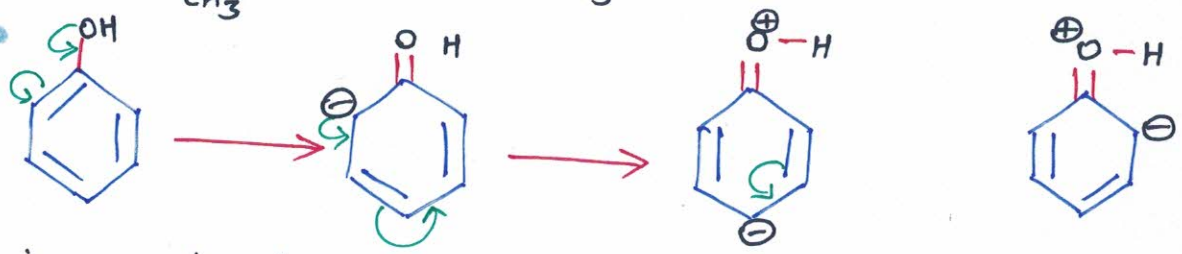
Hyperconjugation is a resonance effect. Resonance effects ortho & para position only.

i.e. ortho & para are more e^- rich. so E^+ goes to ortho or para.

All alkyl groups are ortho para directive groups.



Generally, due to crowding, at ortho para compound are formed.

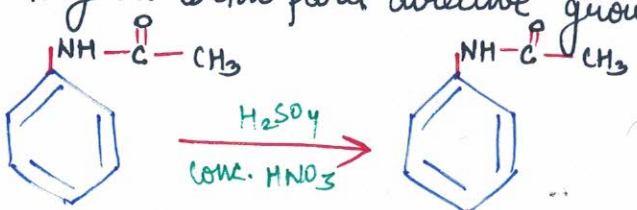


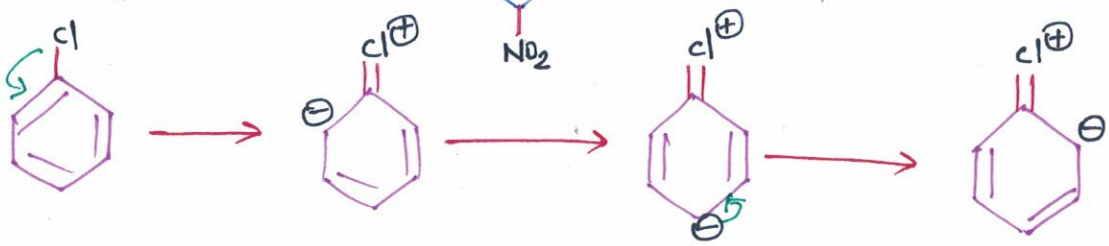
$-OH$ is a great releasing group.

$-OH$ is a ortho para directive groups.

Hence, $-OH$, $-NH_2$, $-OCH_3$, $-\ddot{N}HR$, $-\ddot{N}HR_2$ are good releasing groups.

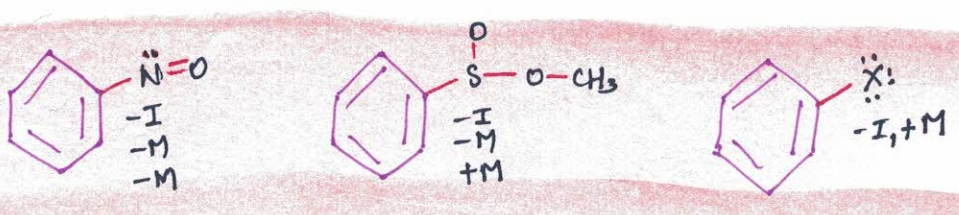
Either by hyperconjugation or +M effect, e^- density ↑ on ring. Thus, rate is ↑, so they are ortho para directive groups.



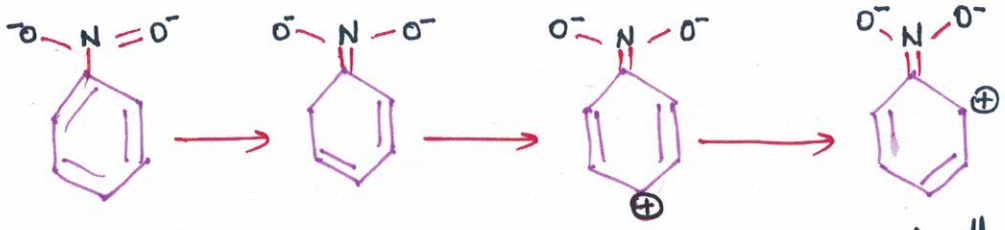


All groups which show +M effect are ortho para directive groups.

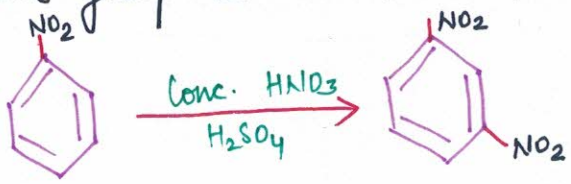
A withdrawing group which can show +M effect are ortho para directive. But rate of decreased in this case.



All are ortho para directive groups but rate is less then benzene.

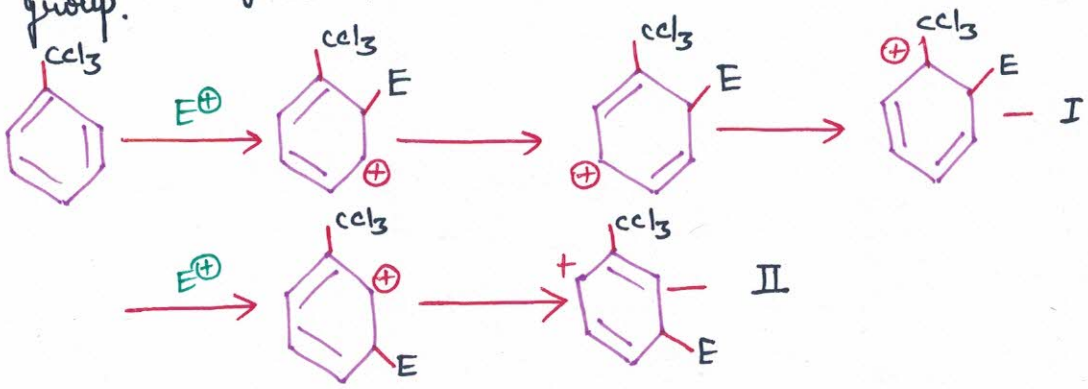


Here NO_2 is a with drawing group which shows (-M) effect. Hence in this case ortho & para are e^- deficient. so meta is relatively rich. so E^- goes to meta position Thus, a group which shows -M effect attached to benzene is a meta directive groups but rate is less than benzene.

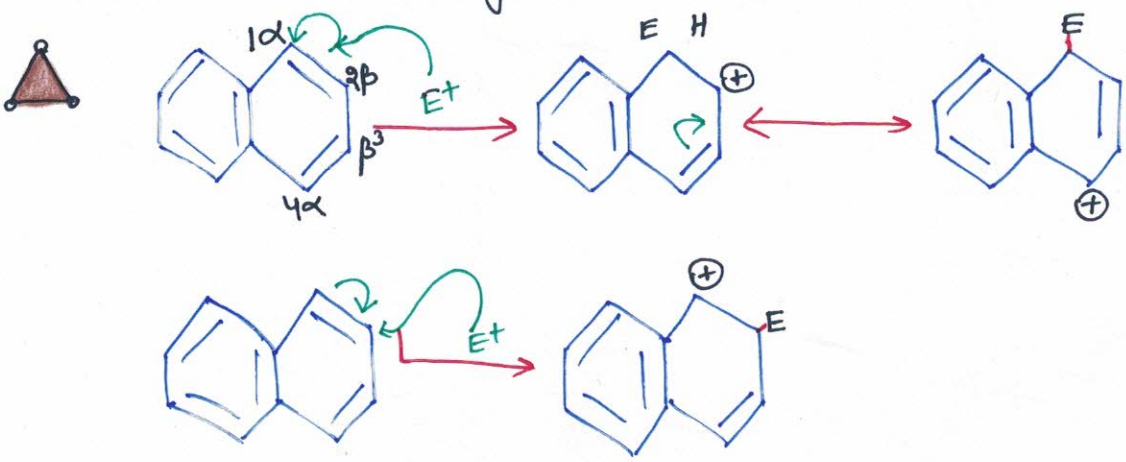


This is a regio selective reactions.

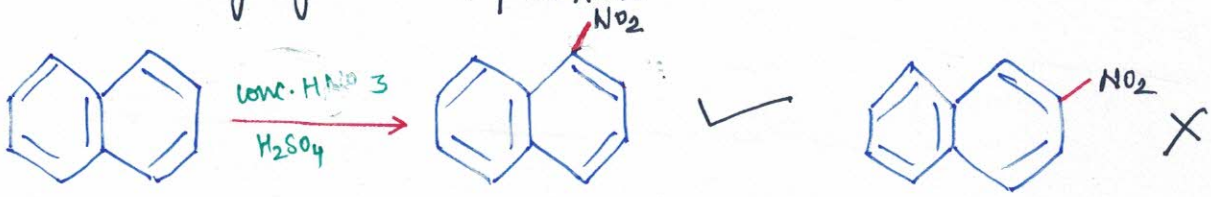
A withdrawing groups which does not show +M effect is a meta directive group.

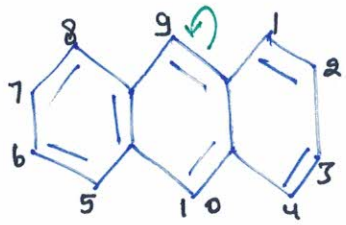


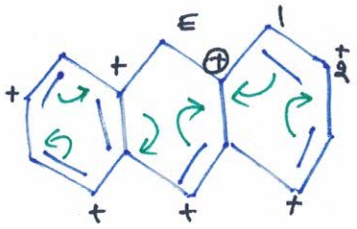
I is highly instable due to withdrawing nature of CCl_3. so "E" goes to meta as it meta as it is relatively more stable than ortho & para.



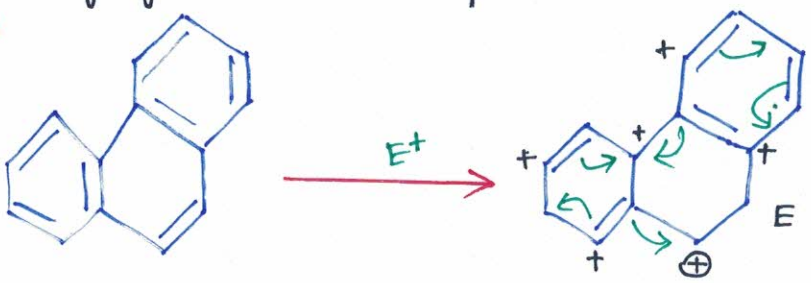
without disturbing aromaticity of other ring. in I^{st} case 2 resonance structures are formed but if E^+ goes to 2^{nd} position only 1 structure is formed. so E^+ always goes to α position.



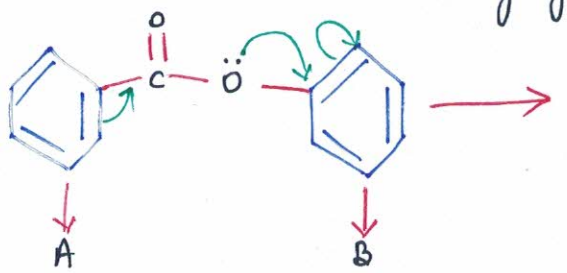




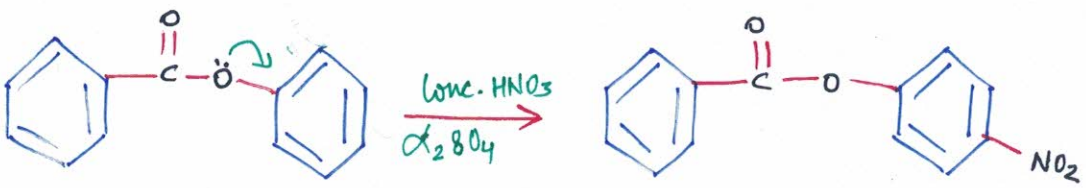
In anthracene 9 & 10 positions are more activated to stable intermediate so, E^+ always goes to 9th & 10th positions.



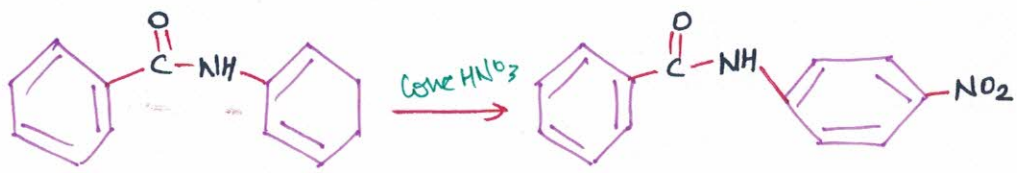
In phenanthracene also, 9th & 10th position are more activated due to more resonance structures so, E^+ always goes to 9th or 10th position.

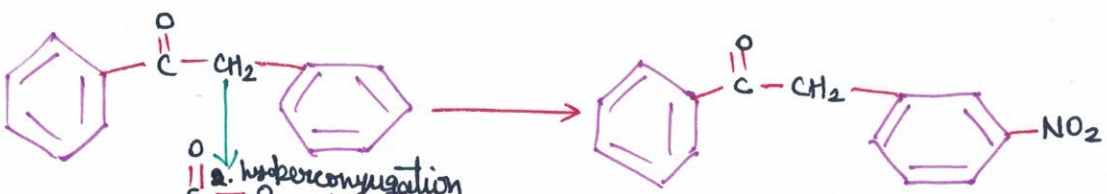


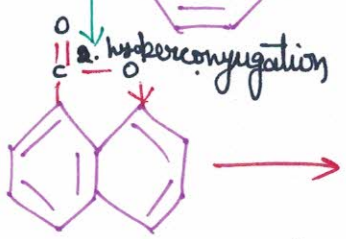
A → deactivated
B → activated
and -O is showing +M effect so E^+ goes to ortho para in B ring.



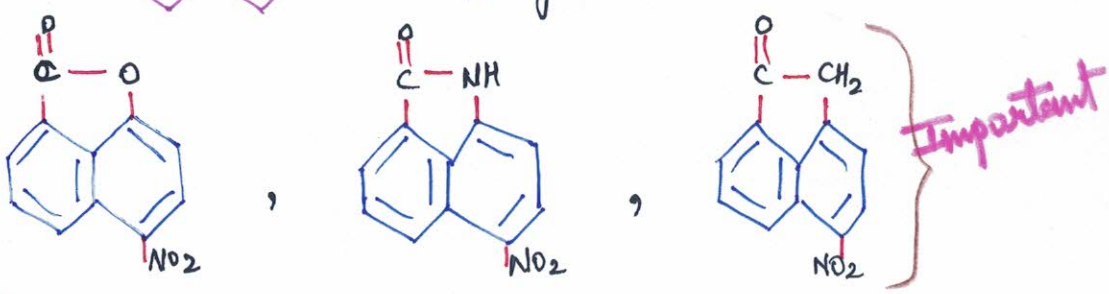
Similarly,



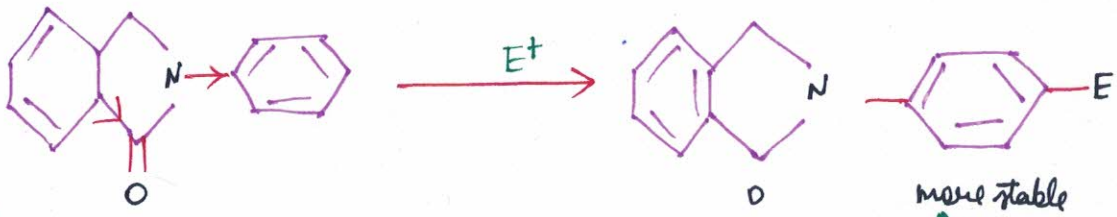


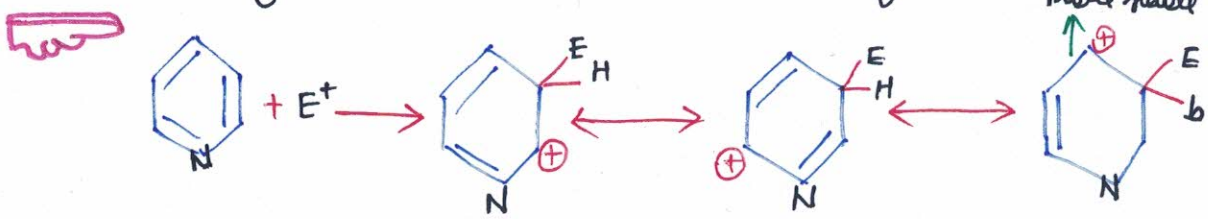


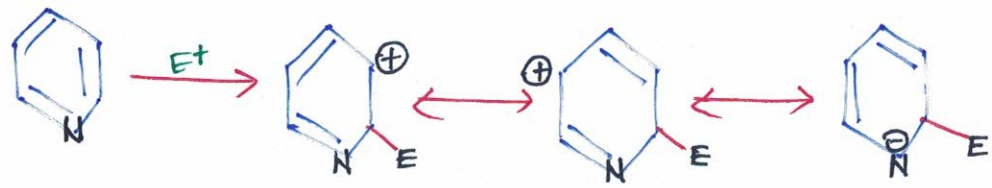
B is activated
E^+ goes to B

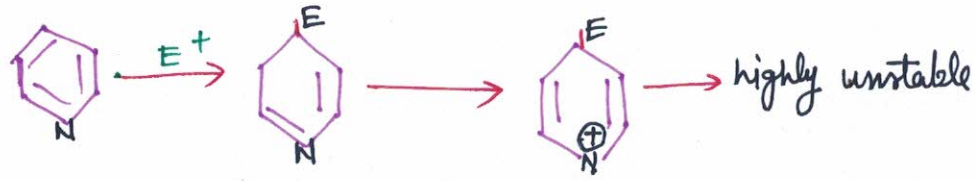


Important

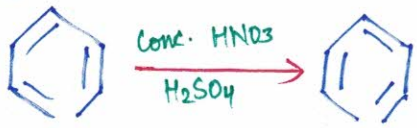


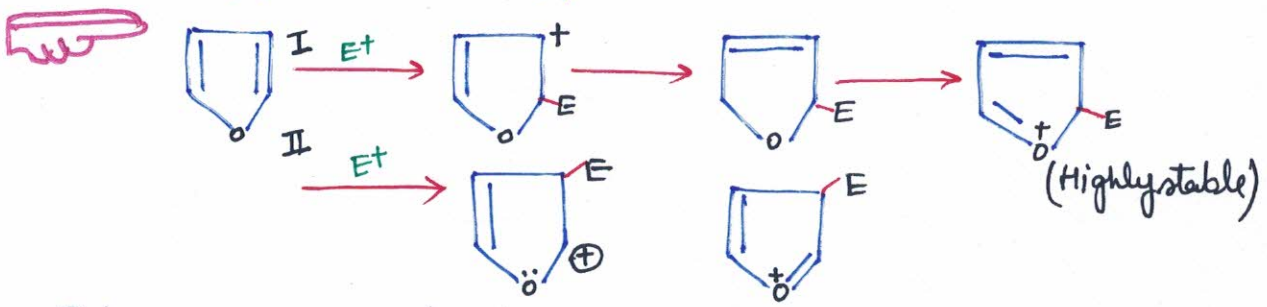




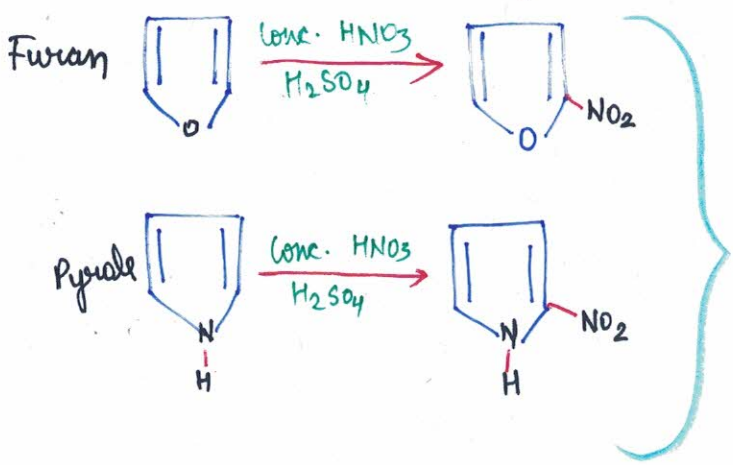


Pyridine is a meta directive group as when E^+ goes to meta, compound is relatively more stable.

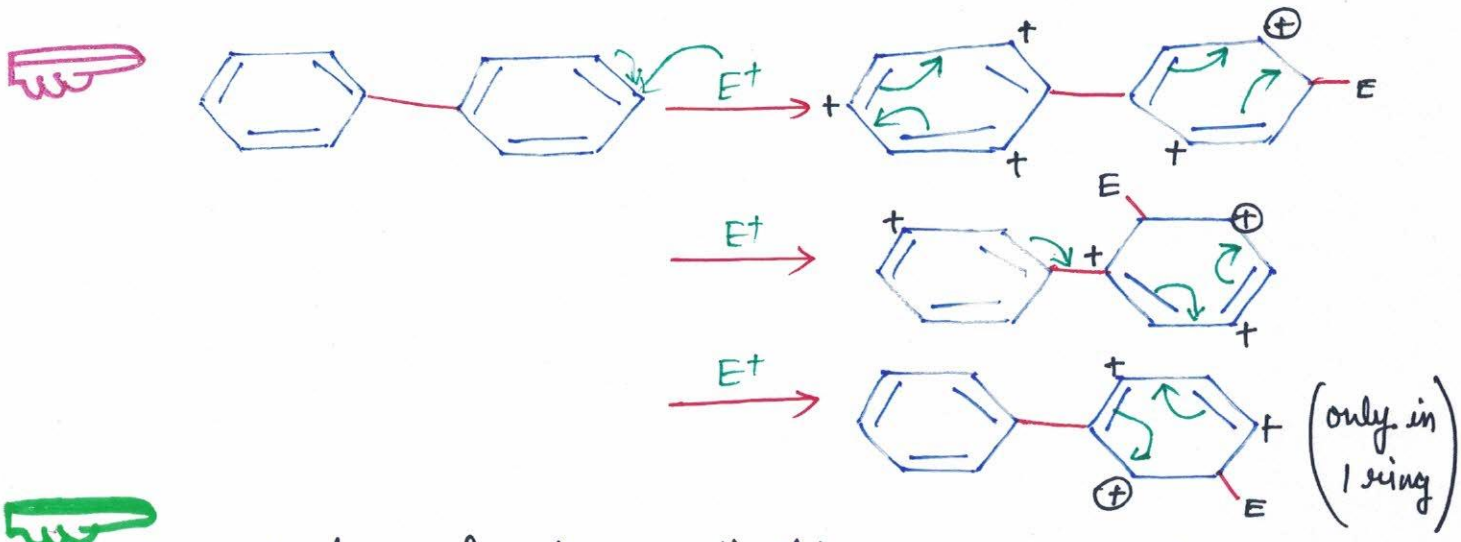




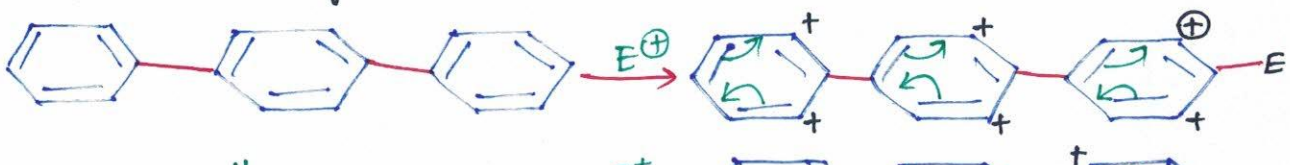
I has 3 resonance structures & II has 2 resonance structures. so I Position more stable and E^+ goes to I.

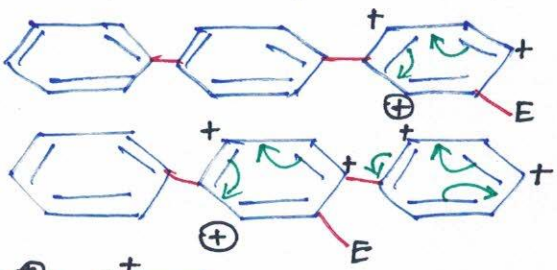


more reactive than benzene as octel complete in these cases.



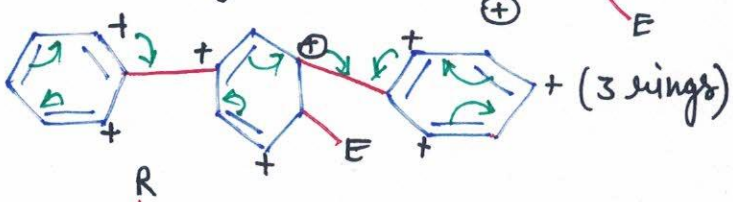
Hence, phenyl group is ortho para directing group as in meta case delocalisation takes place only in first ring and other cases delocalisation is in both the rings.



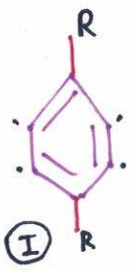


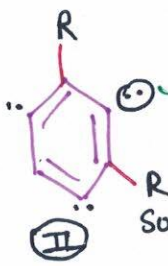
Hence in this case, Ist has max. delocalisation so E$^+$ goes to terminal on the para position mainly.

{E$^+$ gas in IInd ring}



CONCEPT

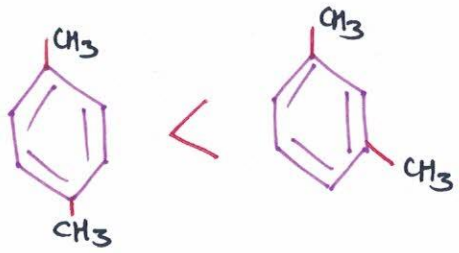




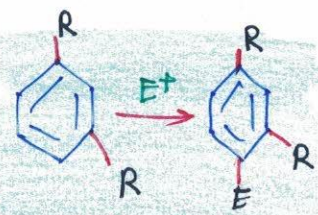
⊙ → crowding.

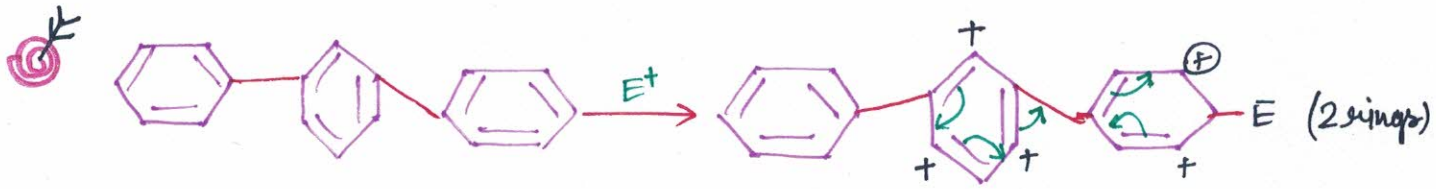
So e$^-$ gas here II is more reactive than I

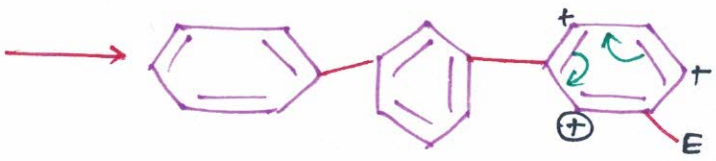
so,



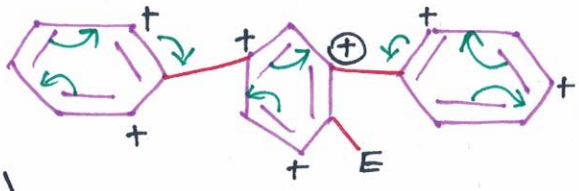
{Rate of Reaction}







{ E^+ goes in IInd ring } →



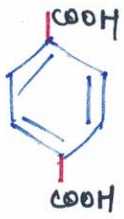
$A\ (C_8H_{10}) \xrightarrow[KMnO_4]{O} B\ (C_8H_6O_4)$

$\xrightarrow[HNO_3]{Conc.\ H_2SO_4} C$ (a single nitro compound)

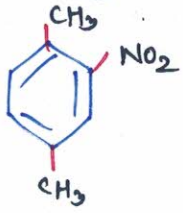
→ whenever mentioned a single compound means groups may be on para positions. As in this case.

A :

B :



C :

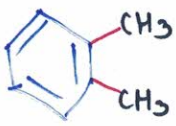


$A\ (C_8H_{10}) \xrightarrow[KMnO_4]{O} B\ (C_8H_6O_4)$

$\xrightarrow{\Delta} C\ (C_8H_4O_3) + H_2O$

→ when on heating anhydride formed, ortho position may be there.

A:



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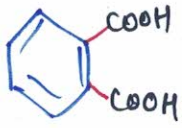

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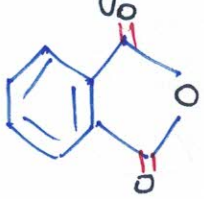
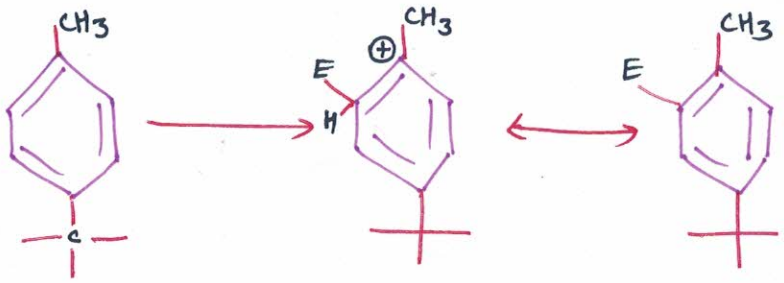
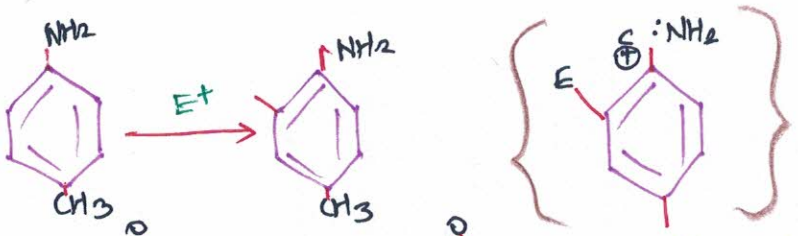
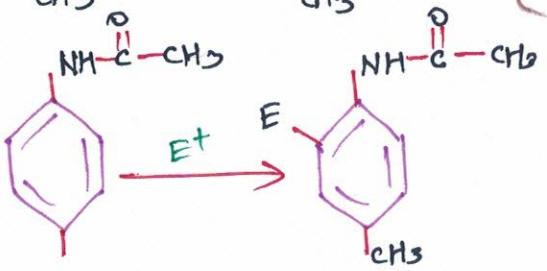
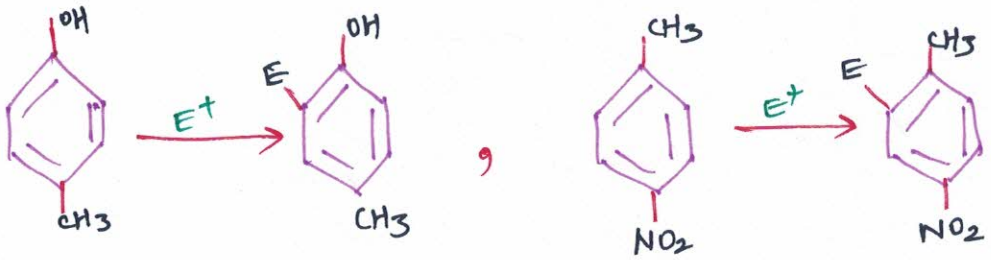
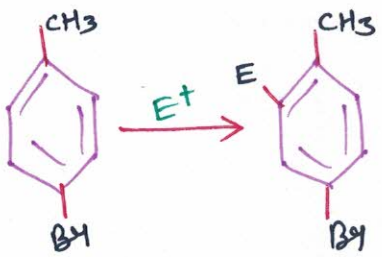


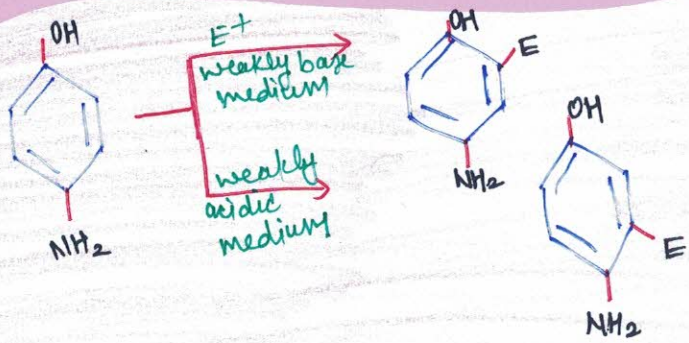






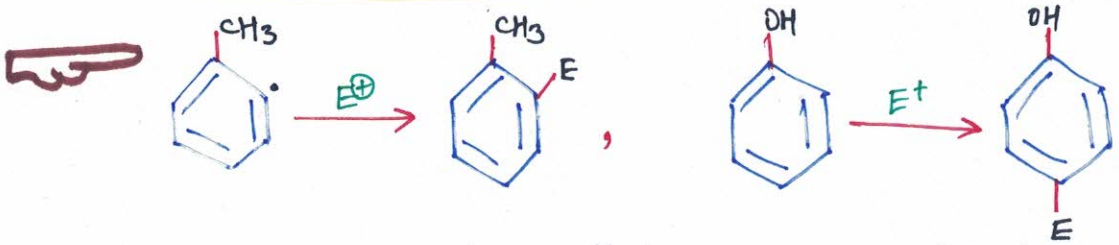




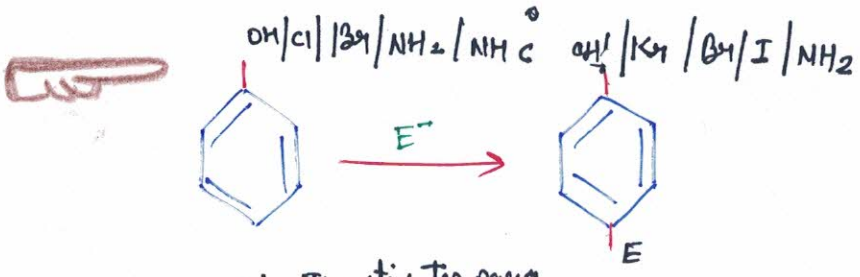


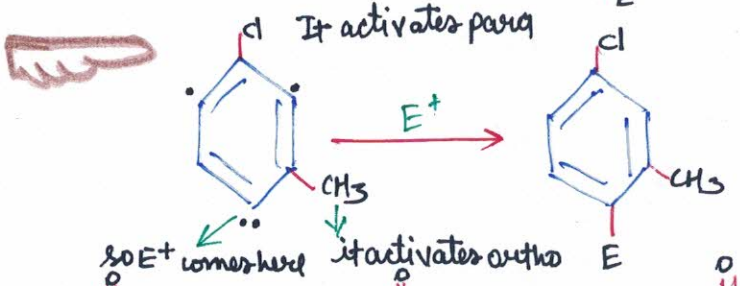
In basic medium, phenol ionises to phenoxide ion which is more good releasing group.

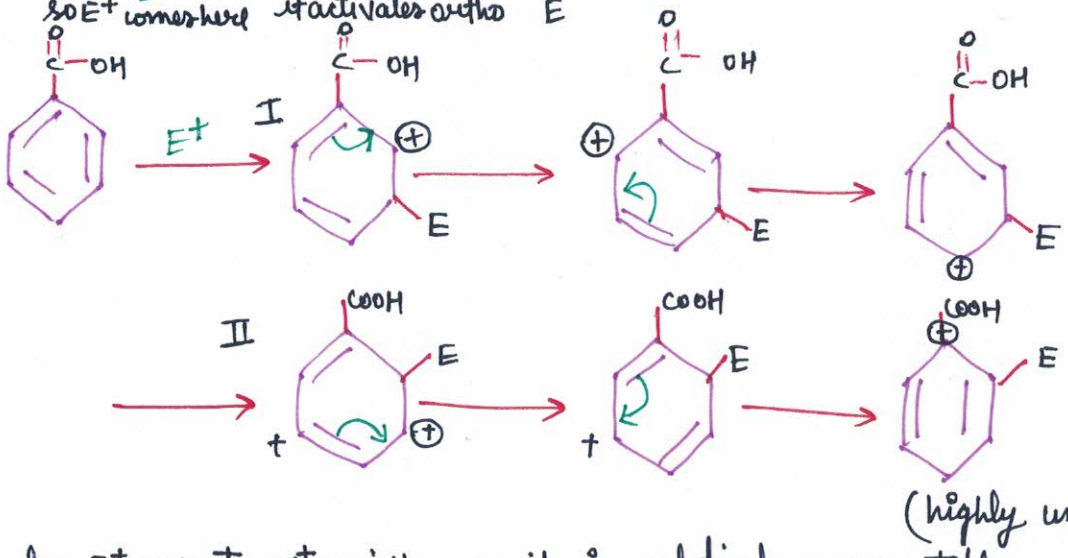
In acidic medium, no ionisation. so as NH_2 is better releasing group than $-OH$, E^+ goes to $-NH_2$.



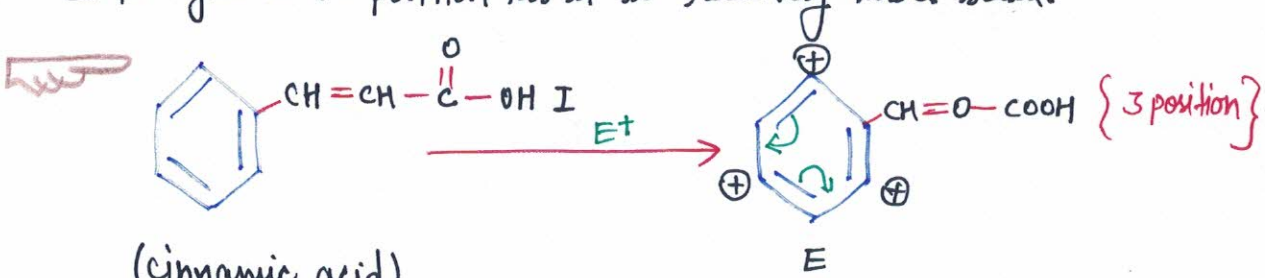
If a group shows $-I$ and $+M$ effect, both para and ortho positions but $-I$ effect is more near. ortho so para is more activated & E^+ goes to para.
But if a group shows $+I$ effect, ortho is more e^- rich than para, so E^+ goes to ortho position.



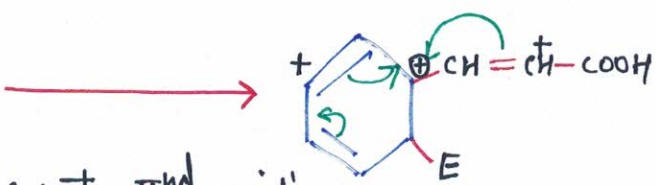




So, E^+ goes to 1st position as it is relatively more stable.



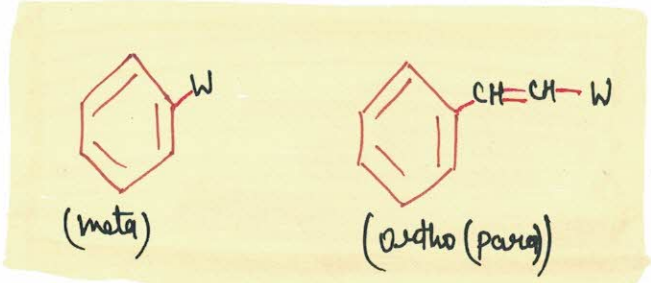
(cinnamic acid)

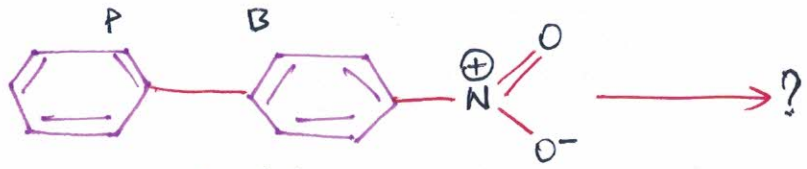


{More delocation in this ring}

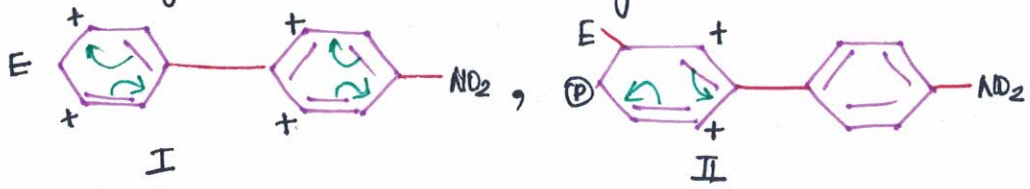
So, E^+ goes to IInd position.

Benzoic acid is a meta directing group cinnamic acid is an ortho/para directing group.





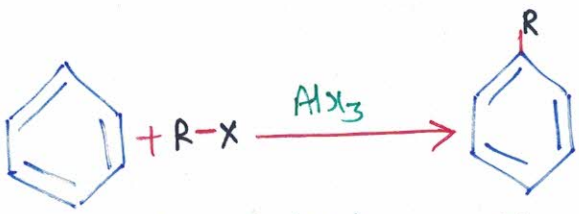
Ring B is deactivated E^+ goes to A.



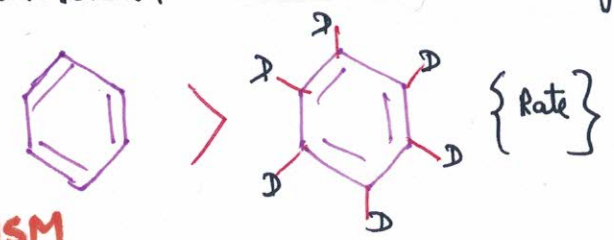
I has more delocalisation than II.

So,

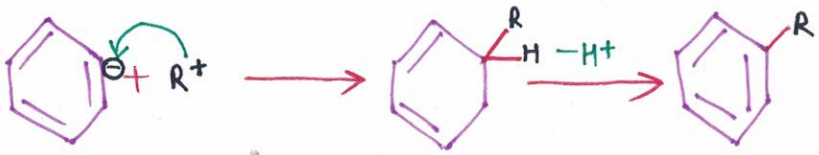
FRIEDEL CRAFTS ALKYLATION
ELECTROPHILIC SUBSTITUTION



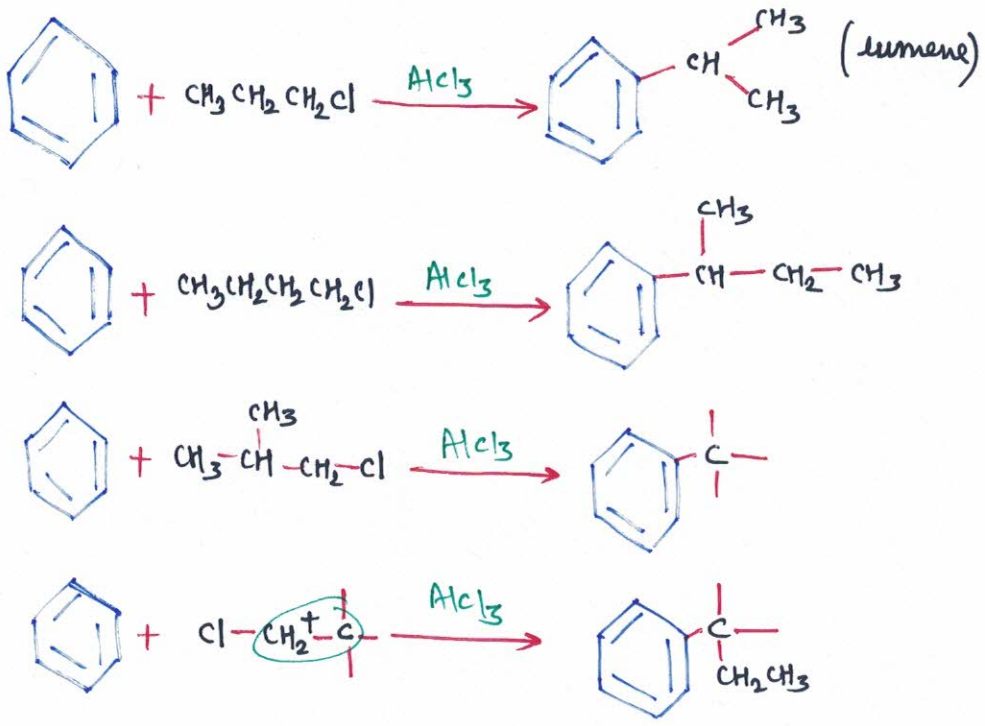
It is an electrophilic substitution reaction and reversible reaction.
As it is reversible, it will show aromatic hydrogen isotopic effect.



MECHANISM



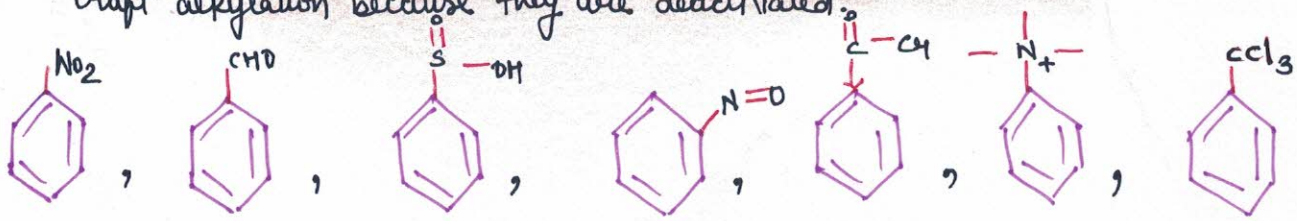
E.g.



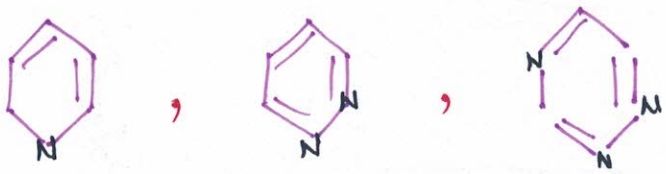
Friedal craft Reaction associate with rearrangement.

The limitation is that it is not possible to prepare linear alkyl benzene as it is undergoes rearrangement.

Rings having withdrawing groups do not undergo Friedal craft alkylation because they are deactivated.



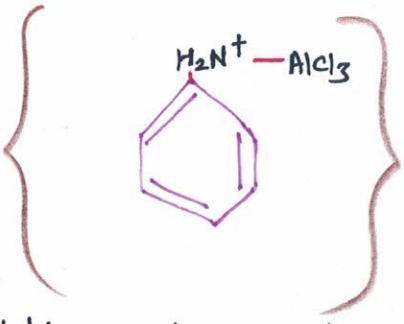
do not undergo F.C. alkylation.



→ do not undergo F.C. alkylation

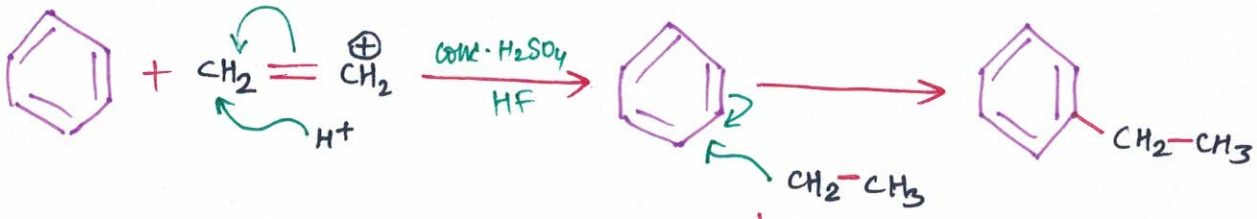
Nitrobenzene is the best solvent for F.C. alkylation because it itself will not undergo alkylation & will also stabilise the intermediate ion as it is polar.

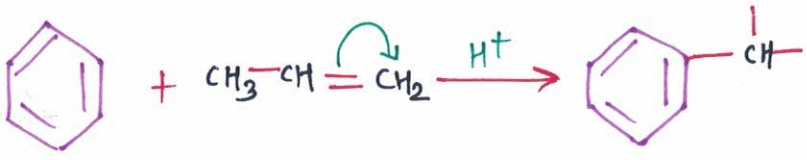
→ do not undergo F.C alkylation because they form a complex with $AlCl_3$ and ring becomes deactivated.

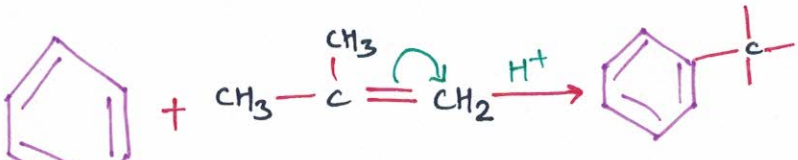


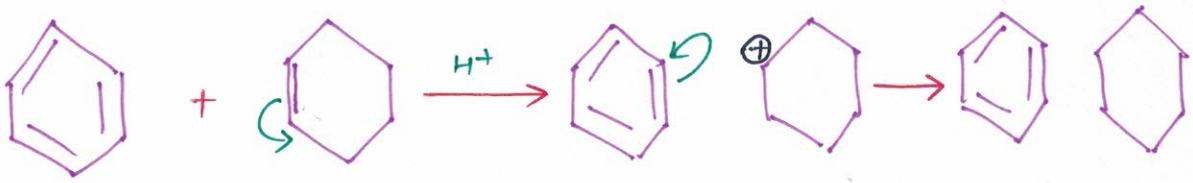
only benzene and alkyl benzene undergo F.C alkylation.

F.C alkylation is also by using an alkene and conc. H_2SO_4 or HF.

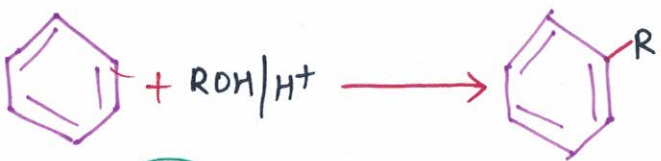


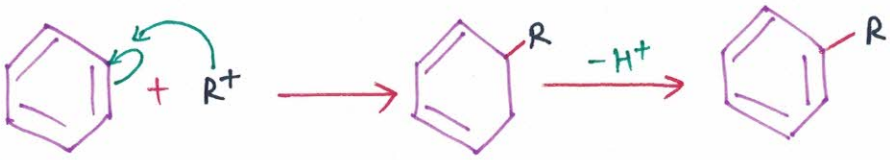


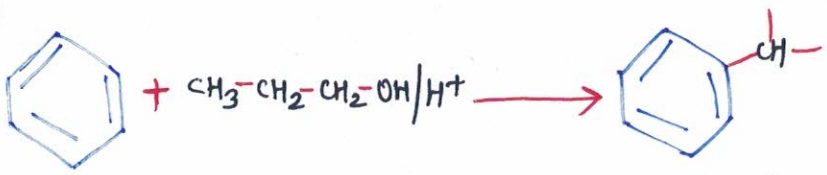


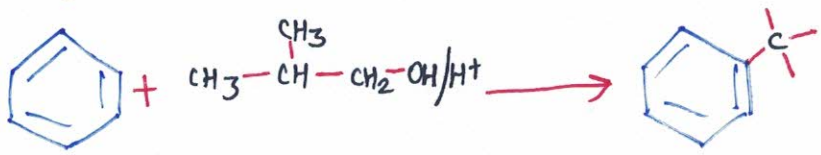


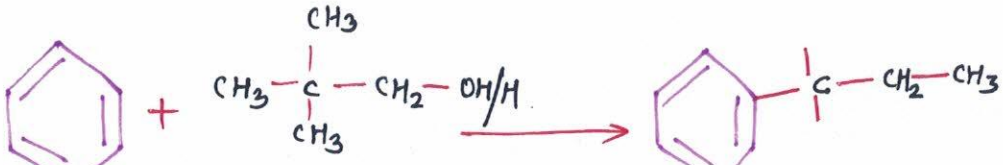
F.C alkylation is also done by using R–OH/H^+

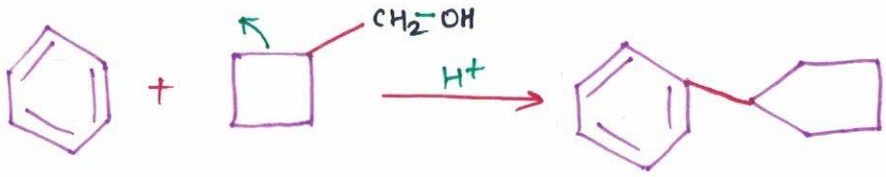


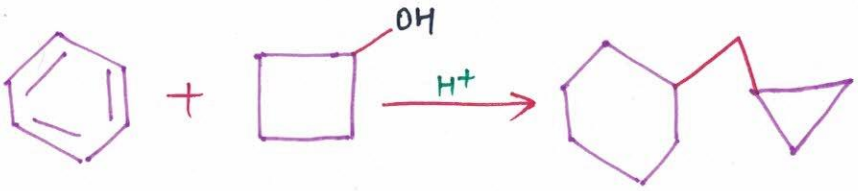










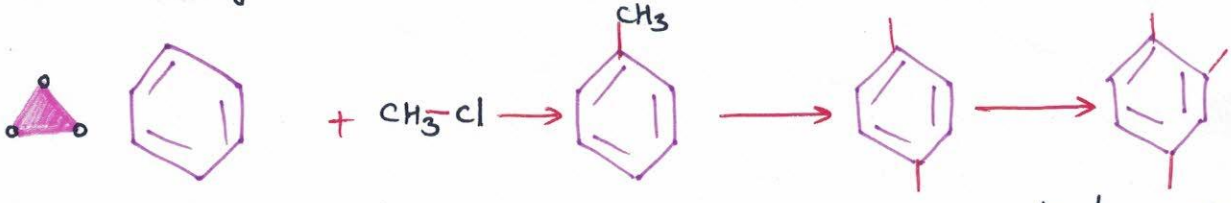


In F.C alkylation, both reactant and solvent should be dry (moisture dry) because if there is moisture then $AlCl_3$ i.e lewis acid react with H_2O and reaction does not take place as catalyst is destroyed.

$$X \xrightarrow[FeCl_3]{AlCl_3} Y$$

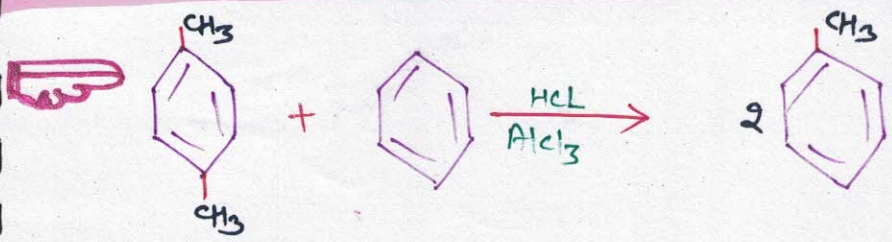
If H_2O present, $AlCl_3 + H_2O \longrightarrow Al(OH)_3 + HCL$

In any organic reaction, if catalyst is lewis acid then reactant must be dry.

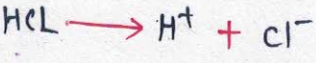


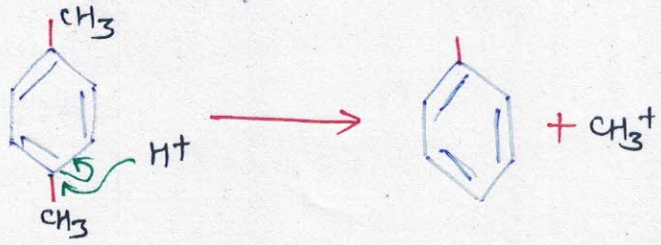
For only mono alkylation to occur, we take the reactant as excess as CH_3^+ collides with more & more benzene forming only mono alkyl benzene.

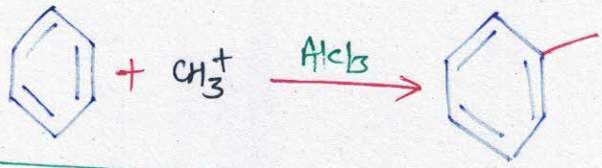
The limitation of F.C is that it is difficult to prepare mono alkyl benzene because if mono is formed, then using ring becomes activated & reaction proceed further and is difficult to stop in the intermediate and reactions becomes fast.

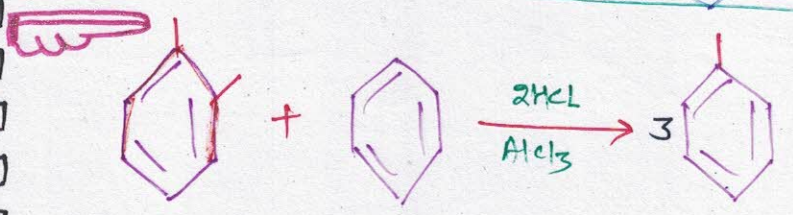


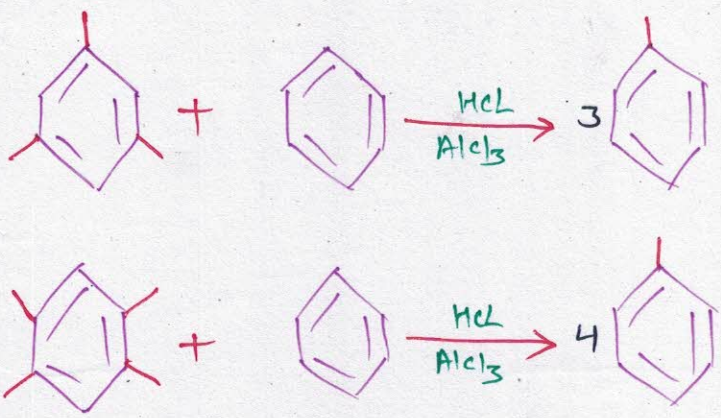
MECHANISM

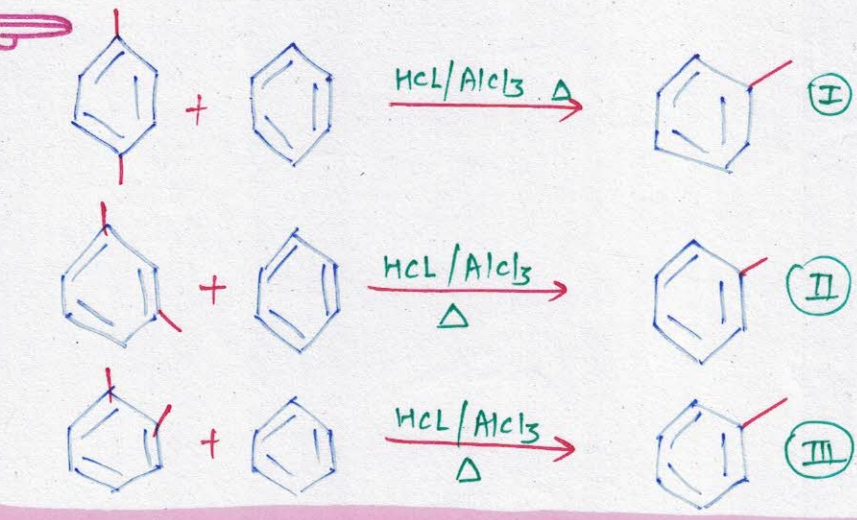




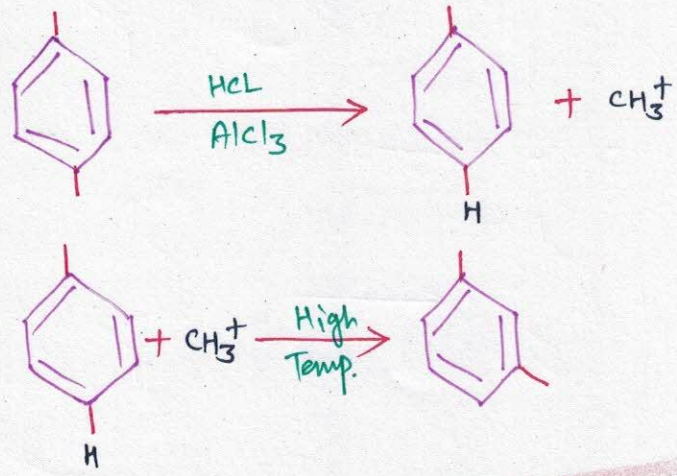


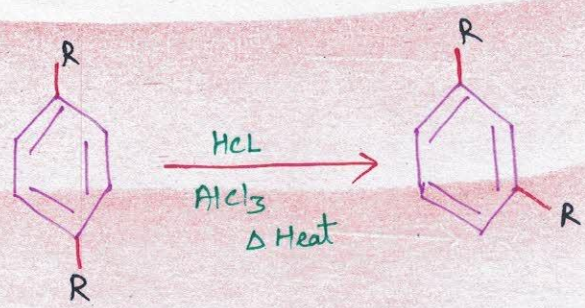


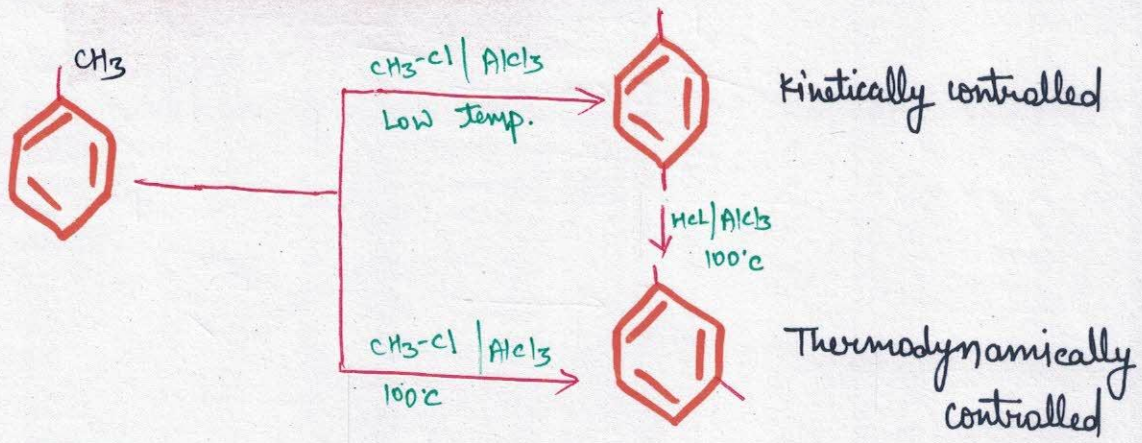


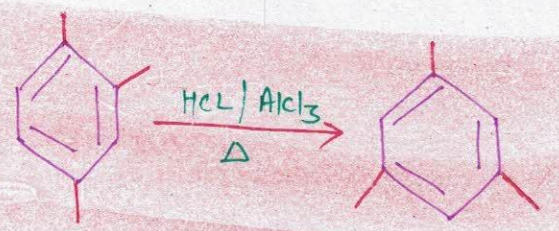


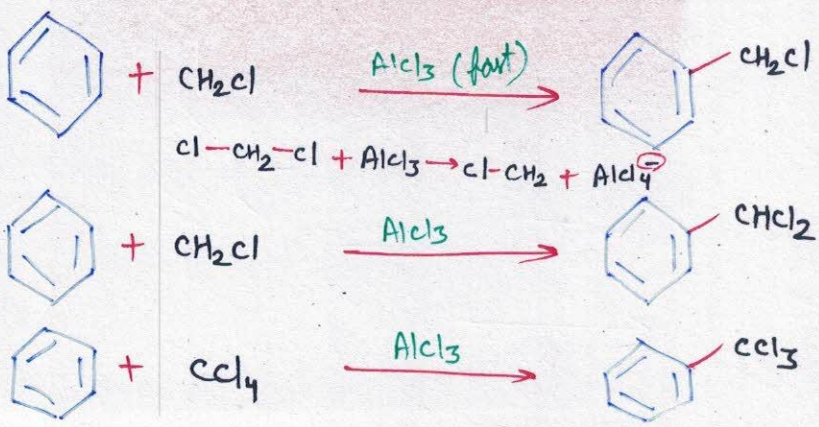
Rate of Reaction ⇒ I > II > III



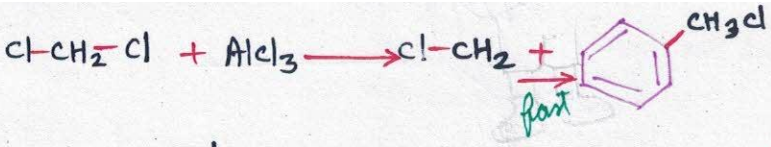


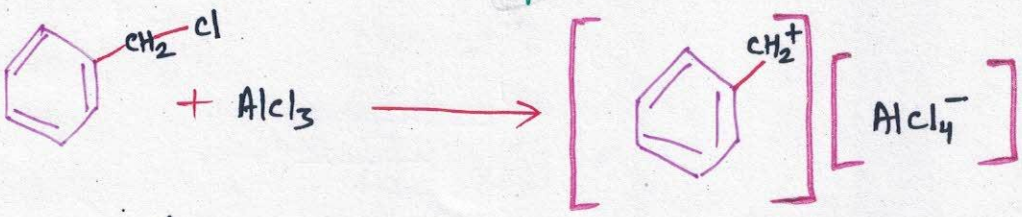




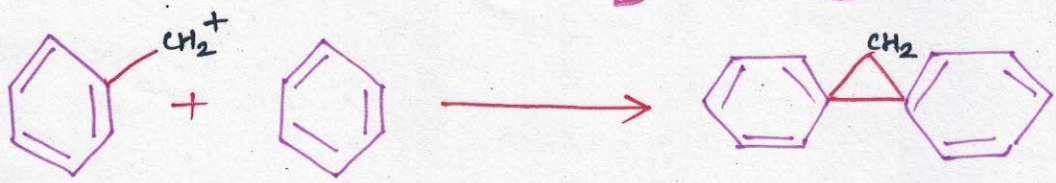


(I) $Cl-CH_2-Cl + AlCl_3 \longrightarrow Cl-CH_2^+ + AlCl_4^-$ (fast)



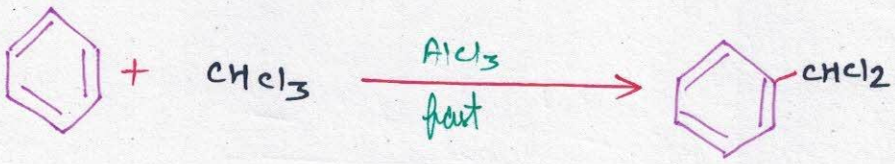


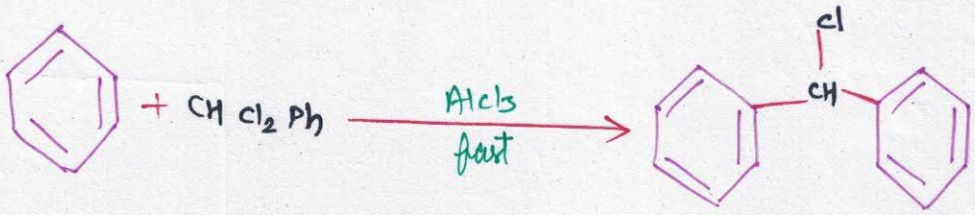
(II)

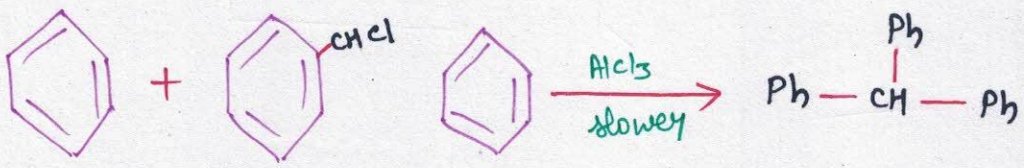


As electrophile is unstable in Ist, rate is fast and electrophile is stable in IInd, " " slow.

Similarly,

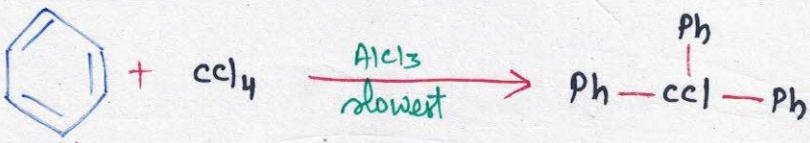


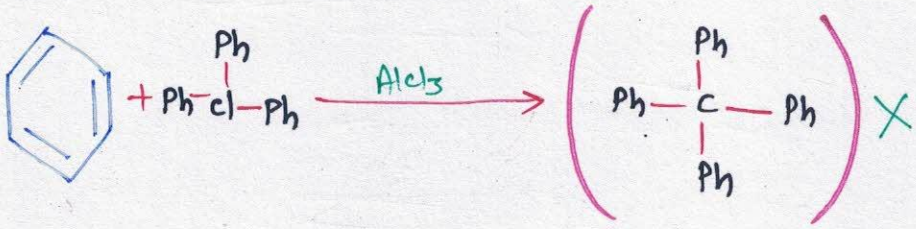




Reaction rate decreases as intermediate becomes more stable.

So,

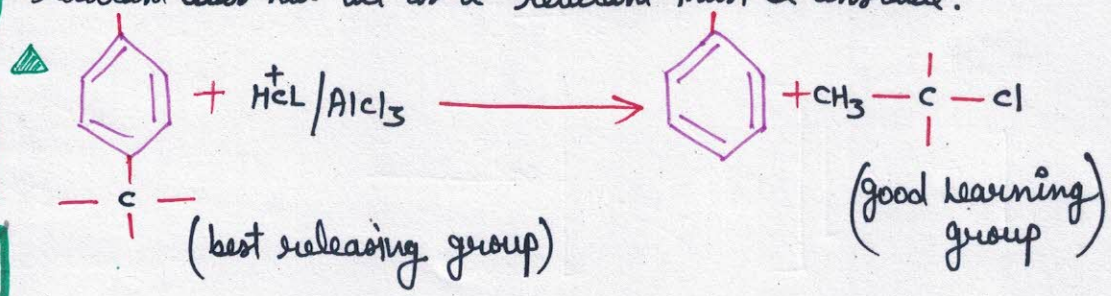


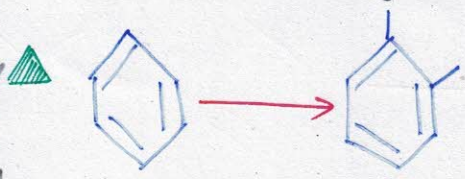


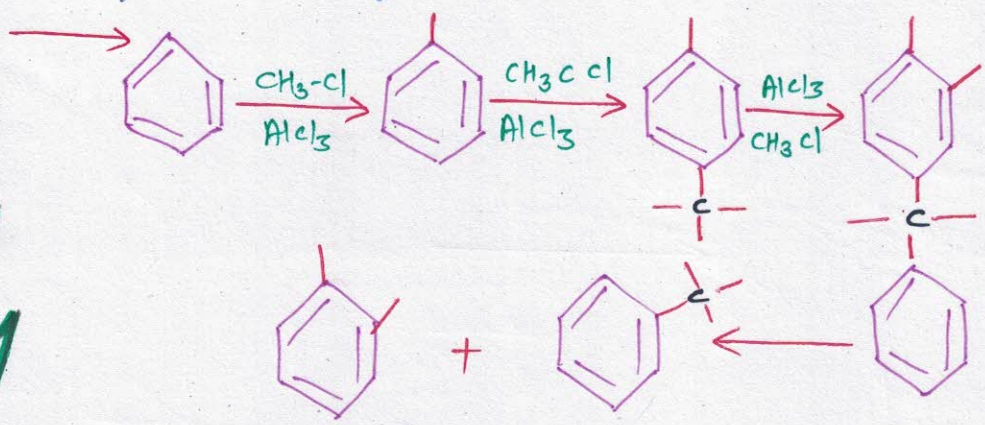
So, No Reaction takes Place.

Does not form

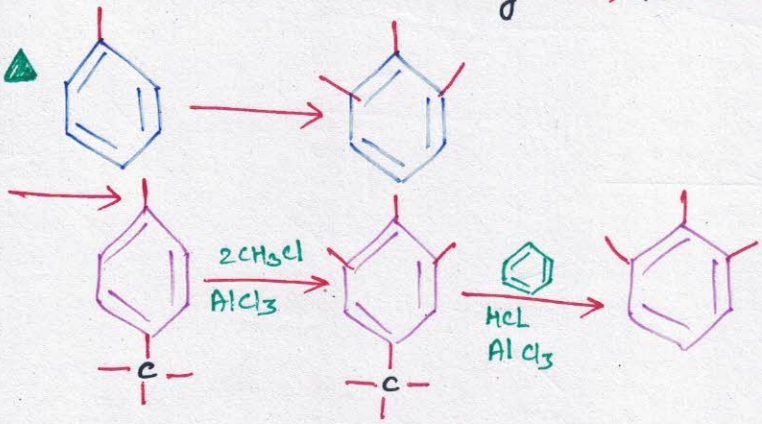
Ph_4 does not exist as the intermediate becomes highly stable and reactant does not act as a reactant must be unstable.

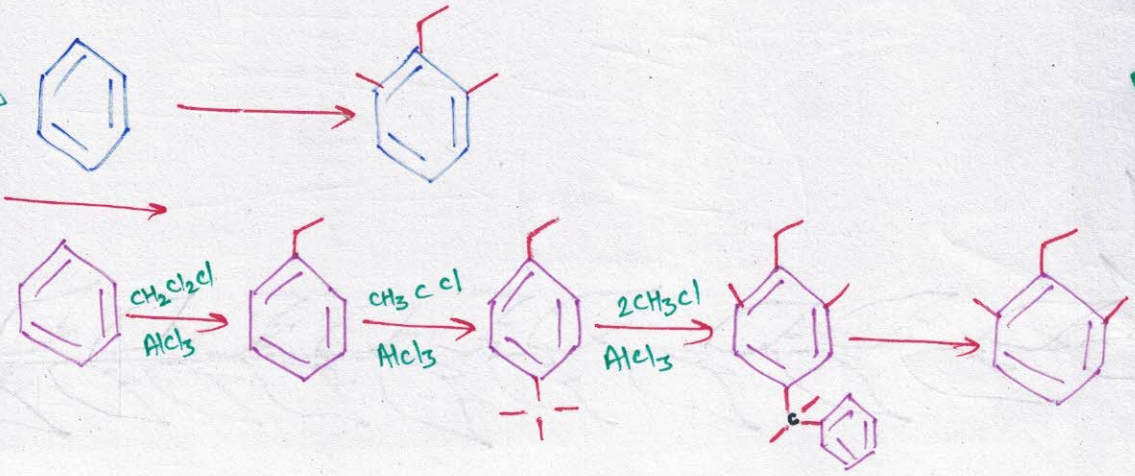


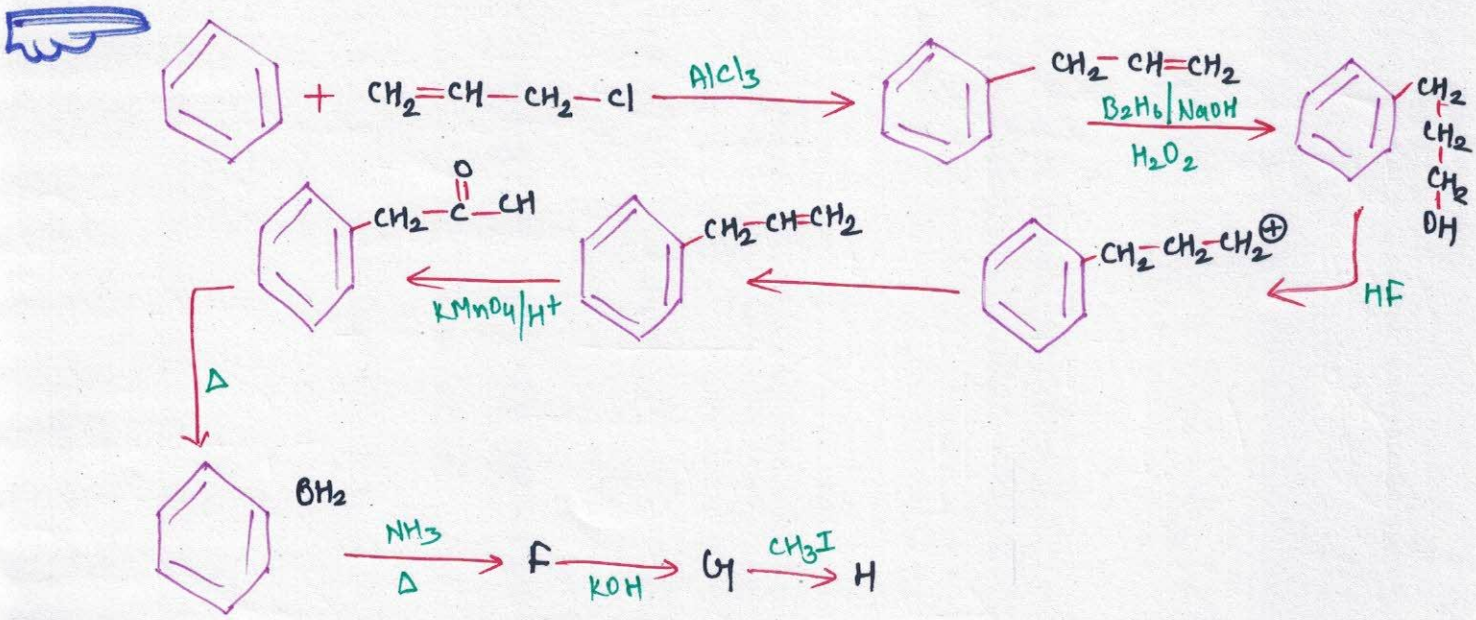


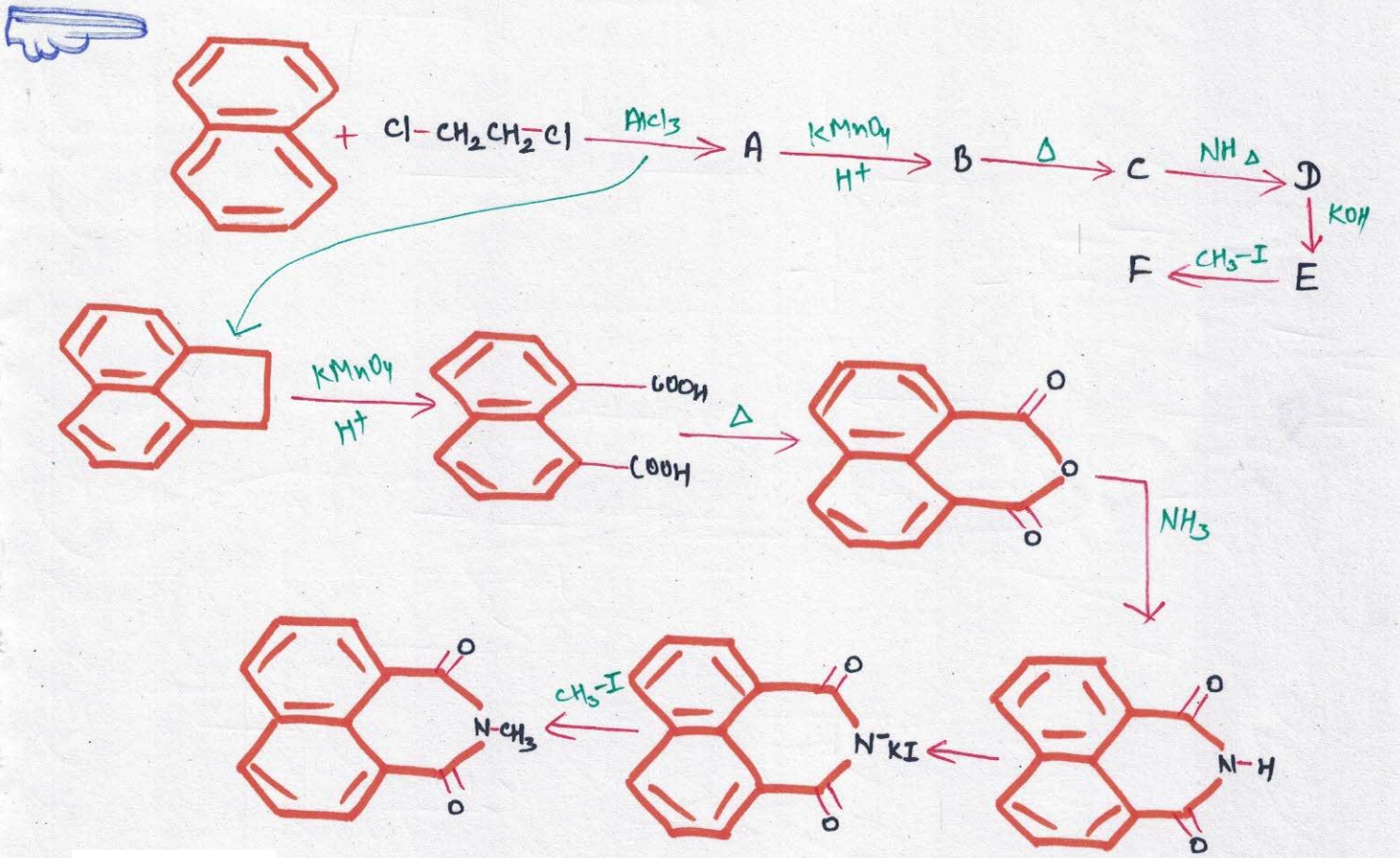


$$R\ MgX + CO_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-O^-MgX \xrightarrow{H_3O^+} R-\overset{O}{\overset{\|}{C}}-OH$$

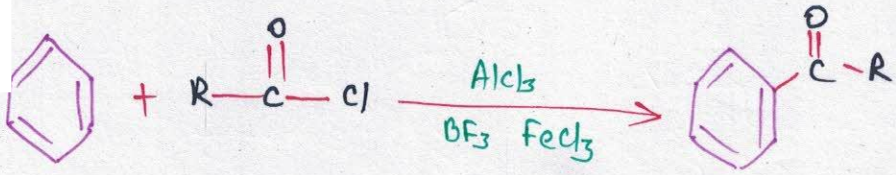




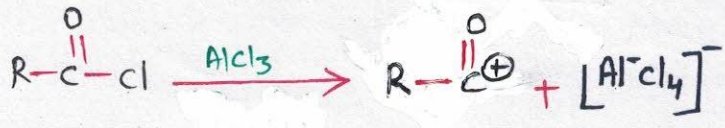


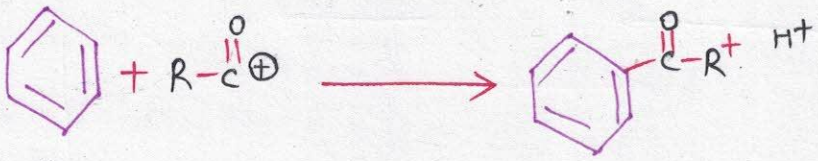


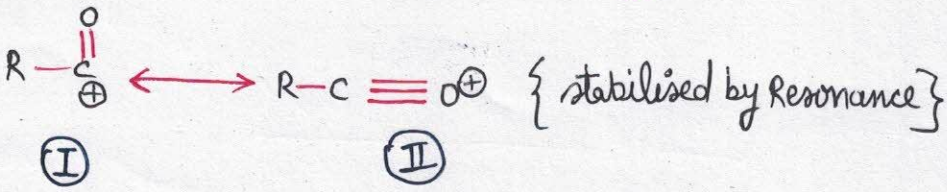
FRIEDAL CRAFTS ACYLATION



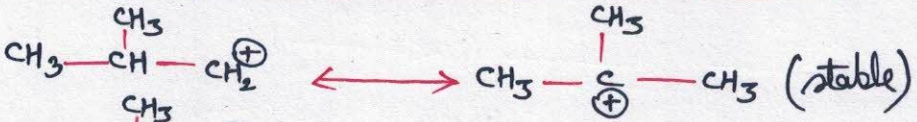
MECHANISM

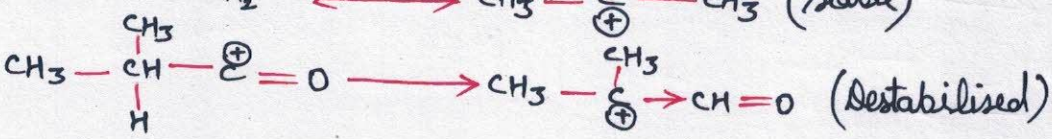






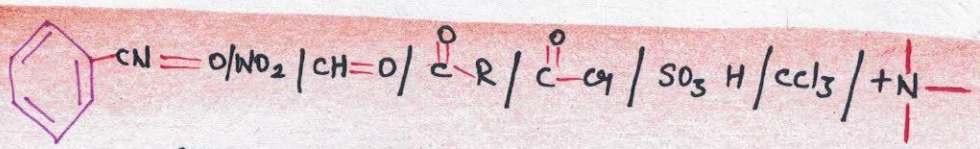
Friedal craft acylation is irreversible.

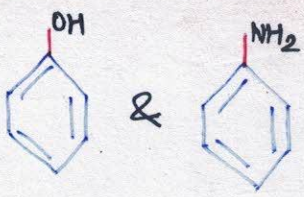
In alkylation, 

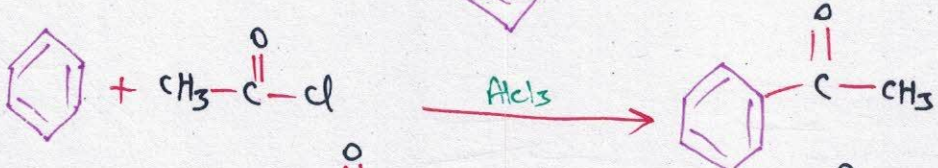
In acylation, 

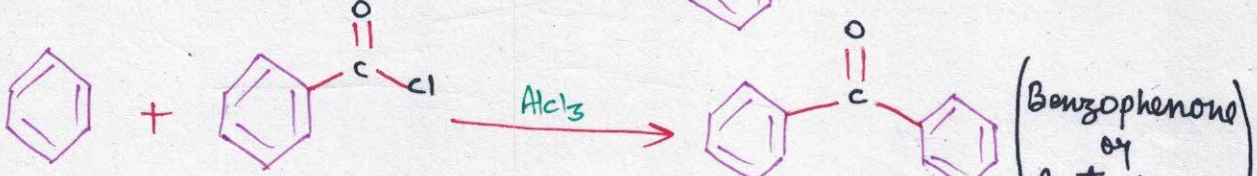
No Rearrangement takes Place in acylation.

Rings having withdrawing groups do not undergo acylation.



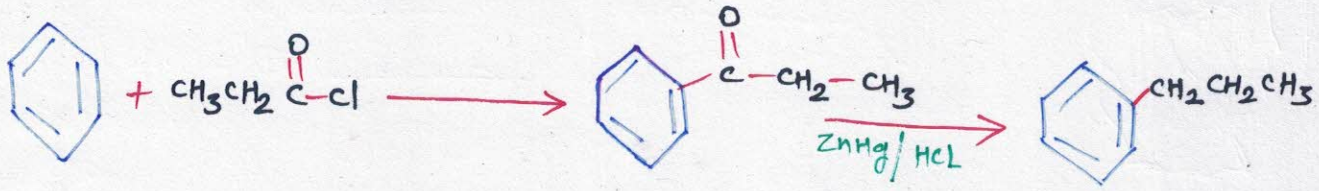
Similarly, 



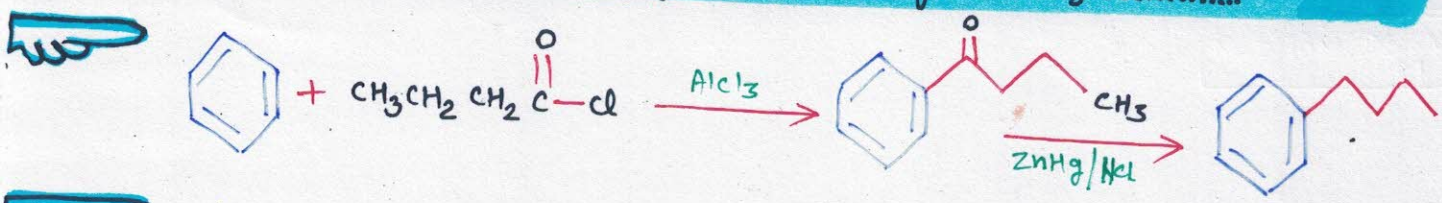


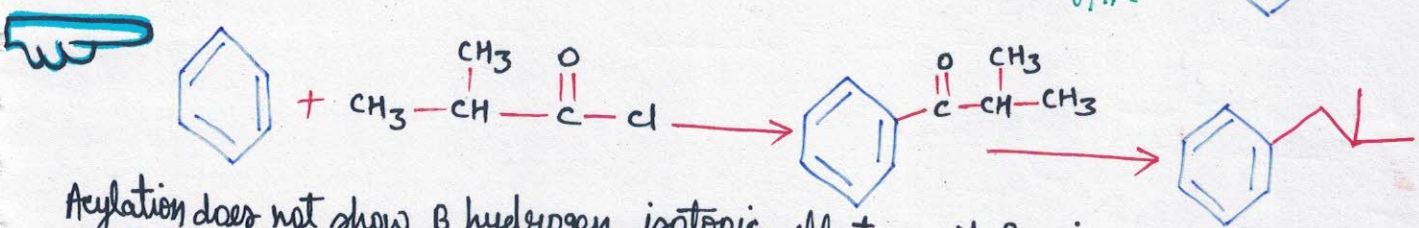
Acylation always occurs at ortho/Para position.

Acylation never occurs at meta as for meta withdrawing group is required and benzene with withdrawing groups acelytion is not possible.

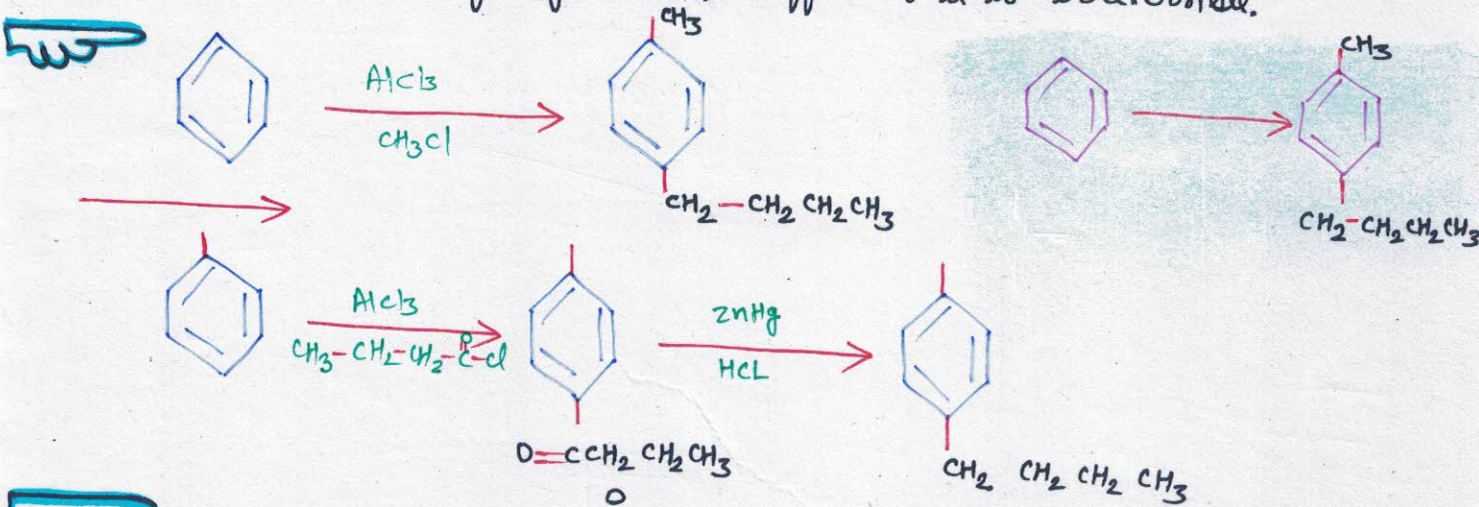


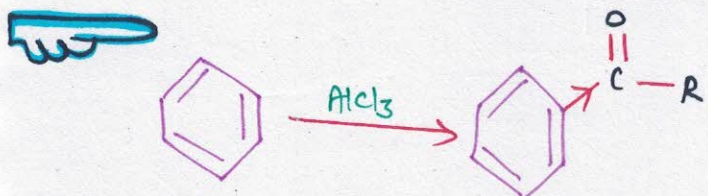
It is a method for preparing linear alkyl benzene.....





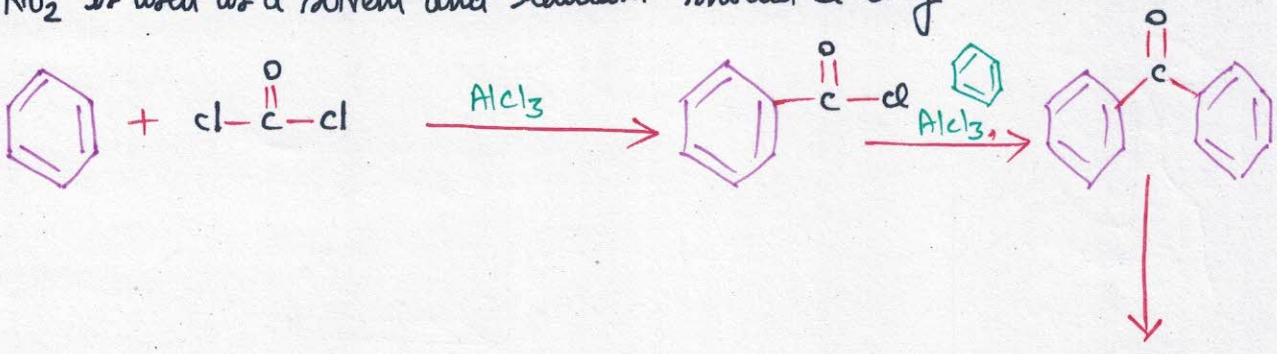
Acylation does not show β hydrogen isotopic effect as it is irreversible.

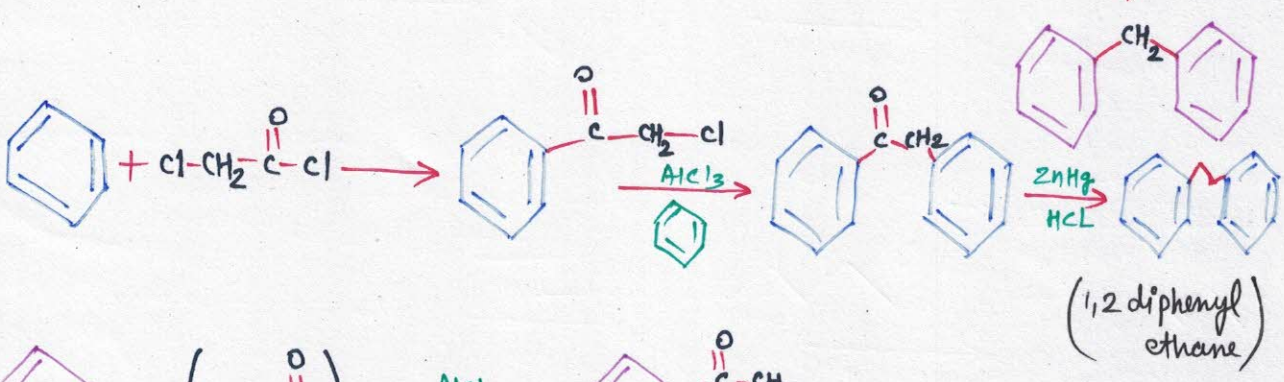




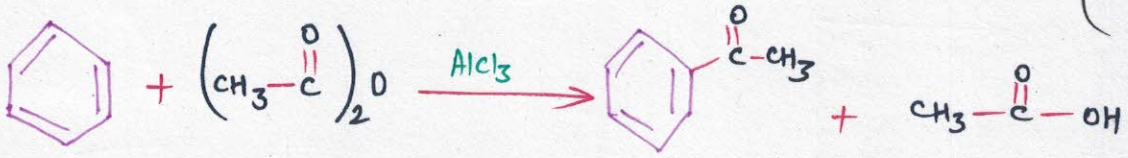
In alkylation it is difficult to form mono alkyl products because ring becomes activated subsequent steps are fast.
But in acylation once acylation is done, $\overset{O}{\overset{\|}{C}}R$ is withdrawing group and ring becomes deactivated after it, no acylation after it.

NO_2 is used as a solvent and reactant should be dry.



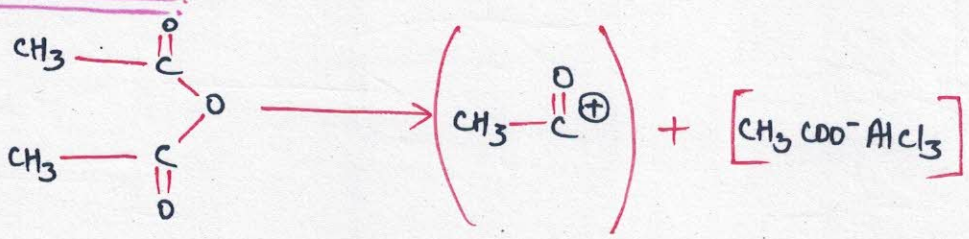


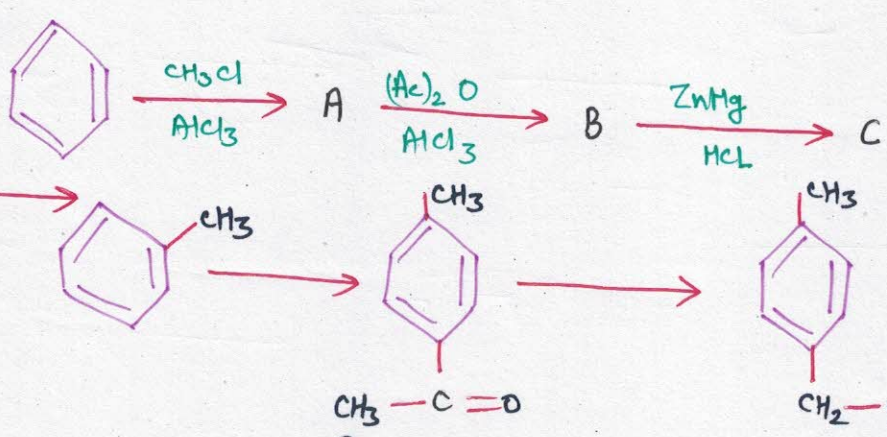
(1,2 diphenyl ethane)

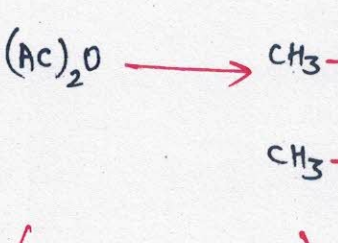


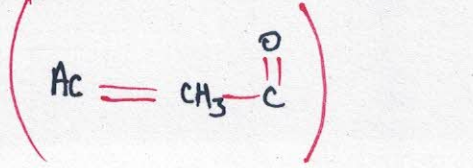
Acylation also done by acid anhydride & lewis acid

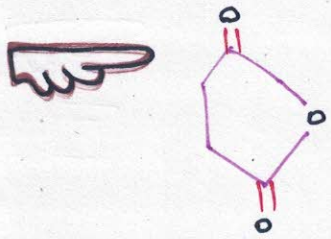
MECHANISM



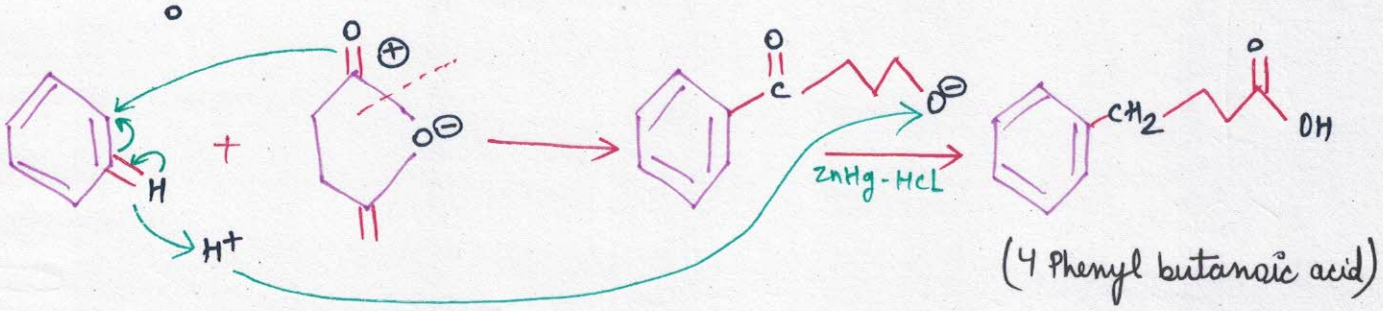




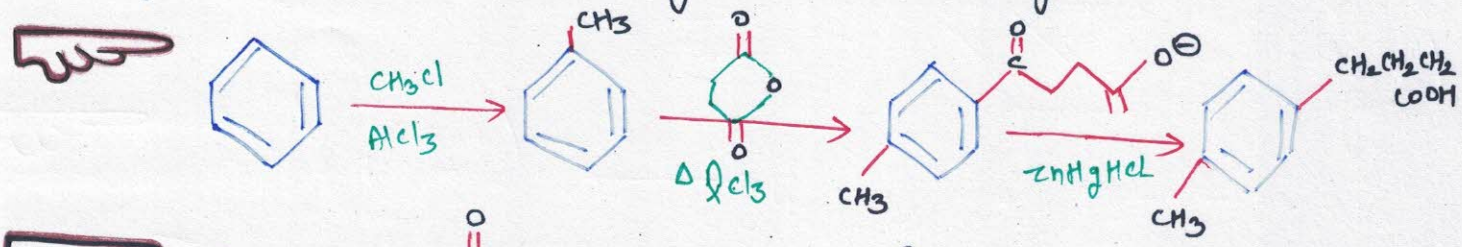


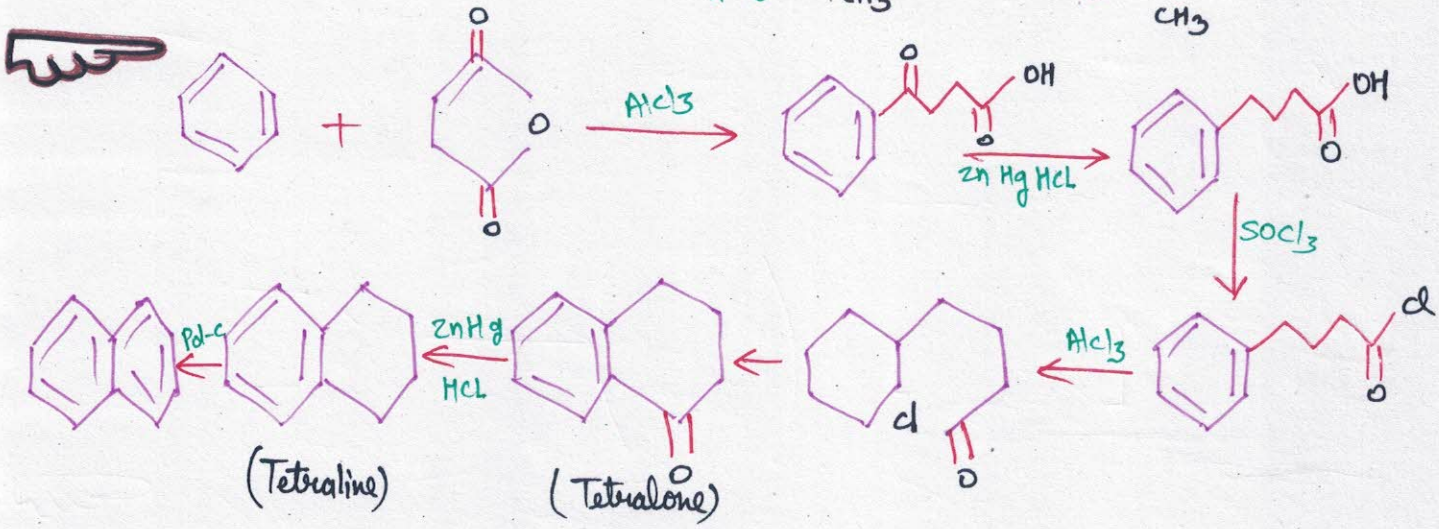


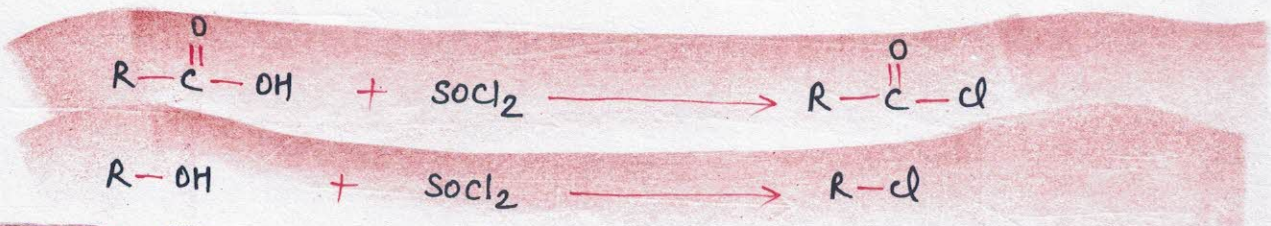
Succinic anhydride

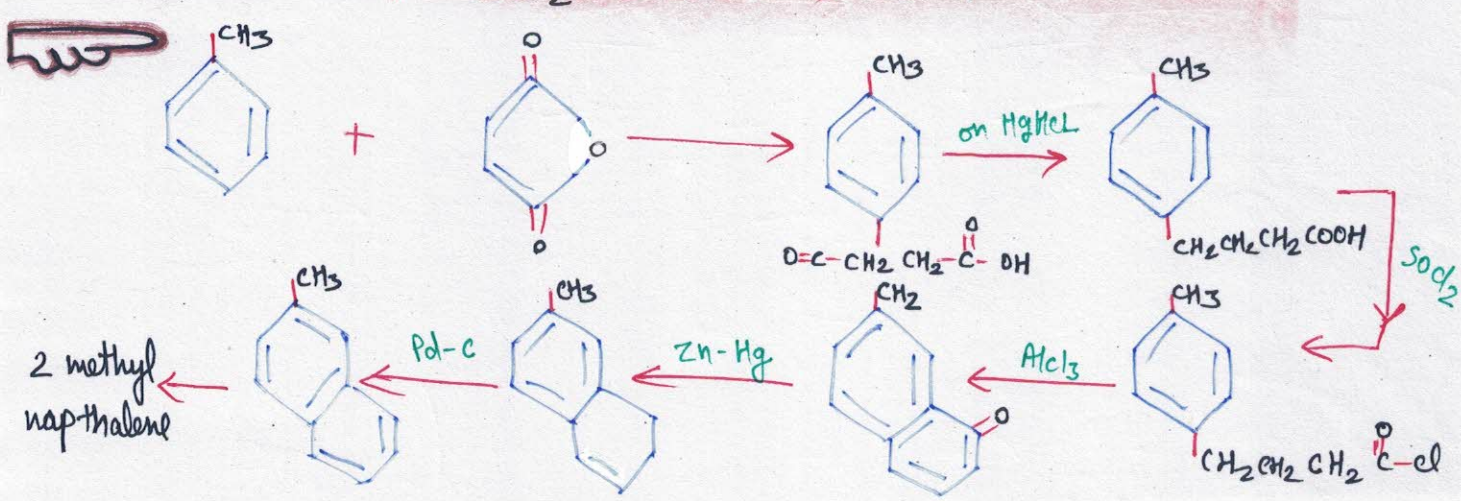


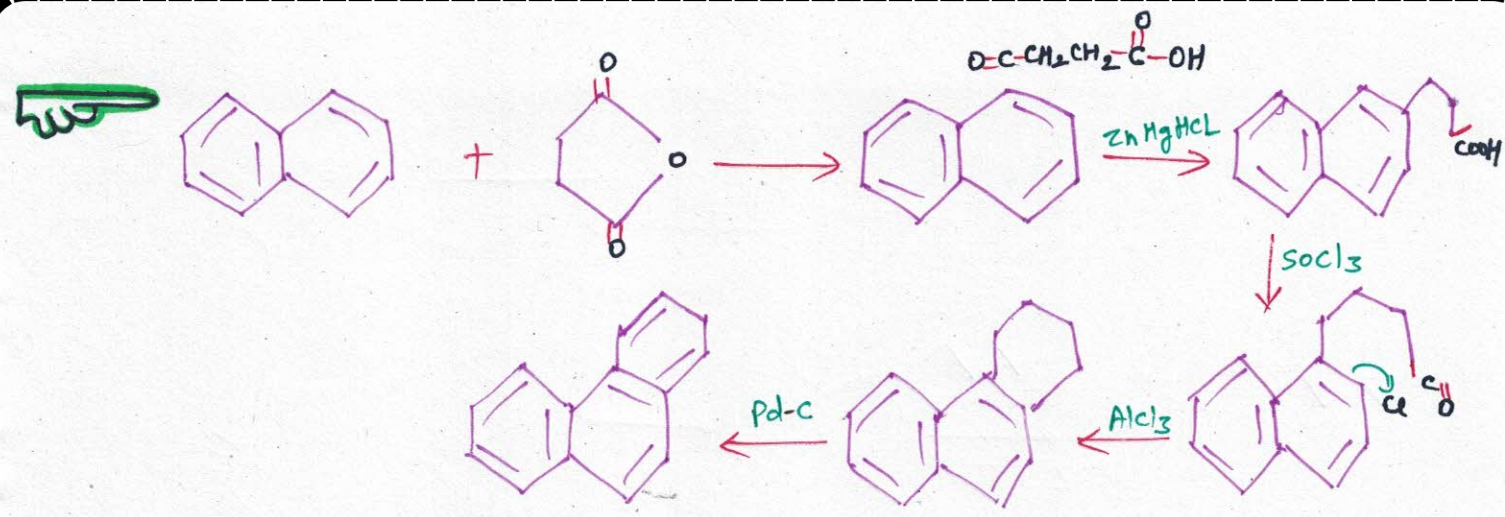
Carboxylic acids are not reduced by clemenson's reagent.



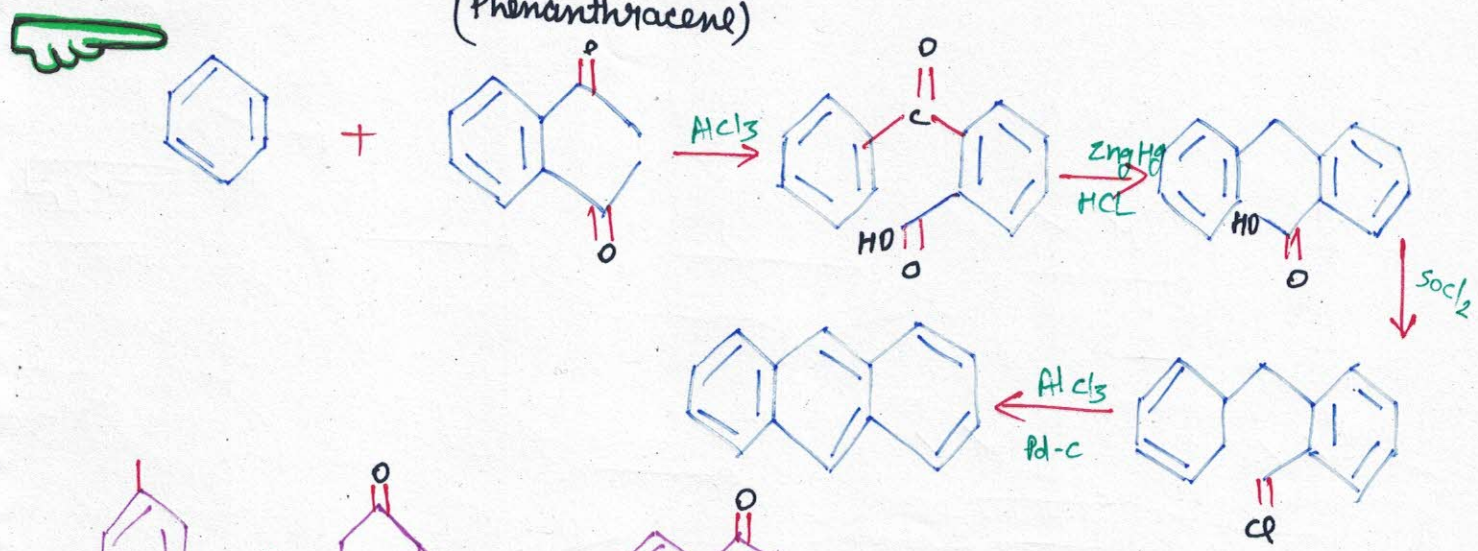


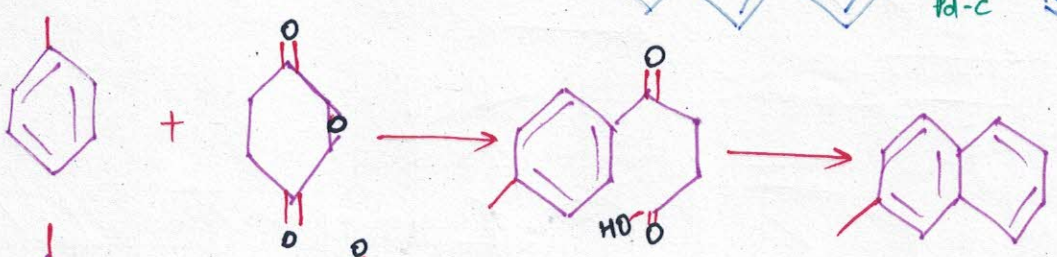


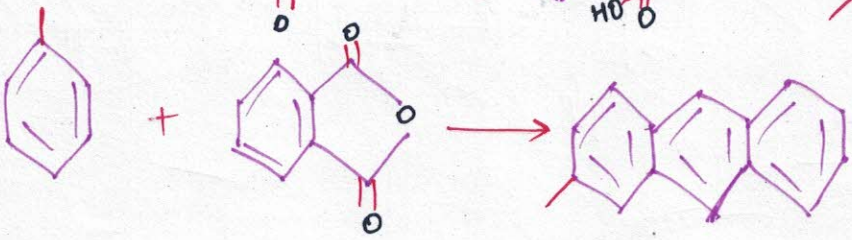




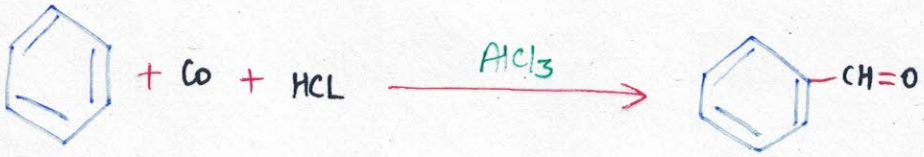
(Phenanthracene)



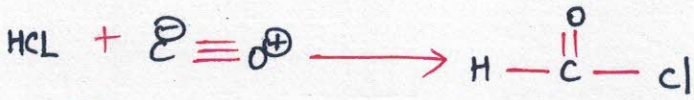


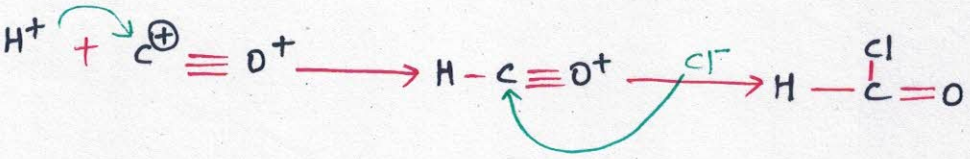


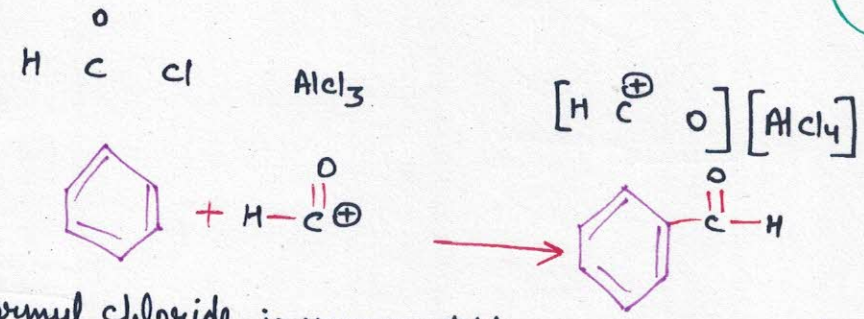
Gattermann-Koch Aldehyde Synthesis



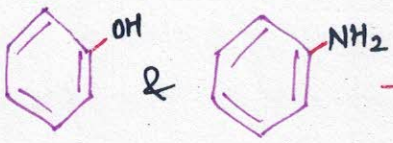
MECHANISM





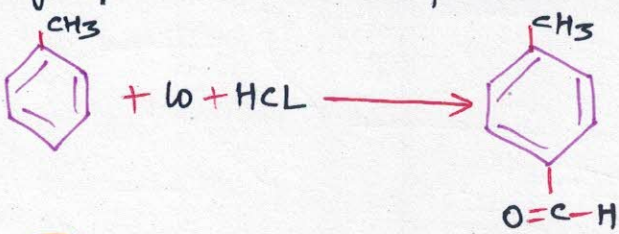


Formyl chloride is very unstable. so it is produced and reacted simultaneously.
Rings having withdrawing groups do not undergo G.K. reaction.
These reactions are irreversible. Hence no β hydrogen isotopic effect.

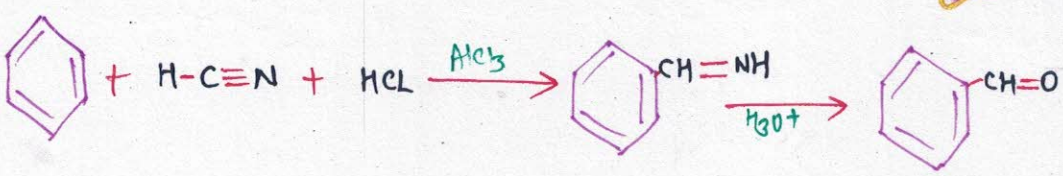


do not undergo G.K reactions.

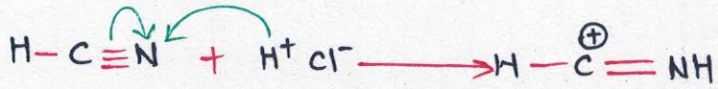
NO_2 group is solvent as it promotes ion formation by providing polar medium.

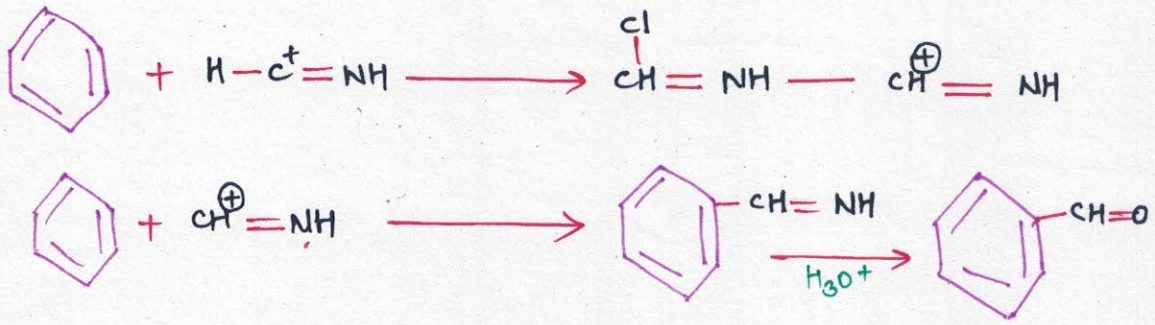


Gattermann Aldehyde Synthesis



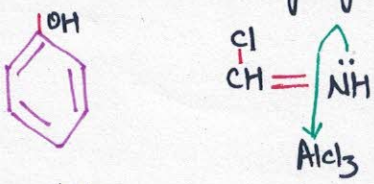
MECHANISM



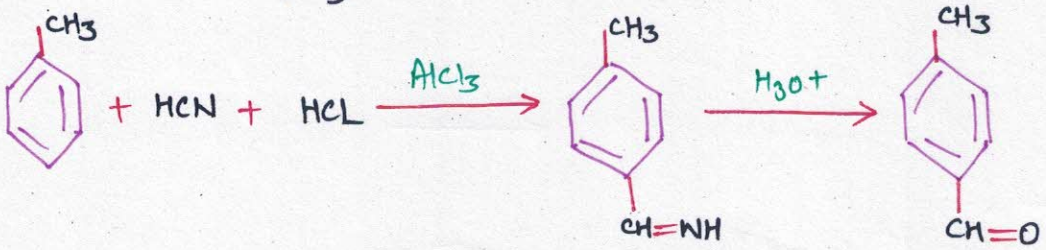


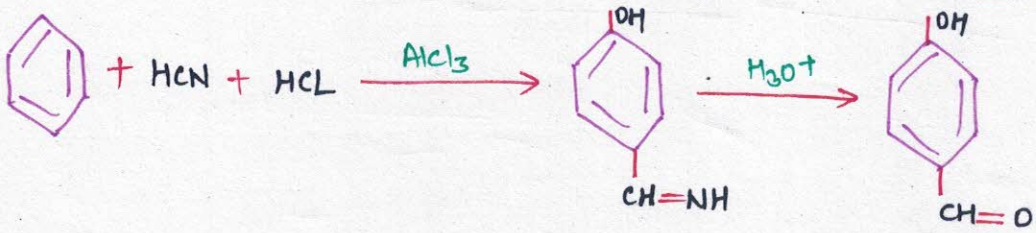
EXCEPTION

Phenols can undergo gattermann aldehyde synthesis and amilies do not



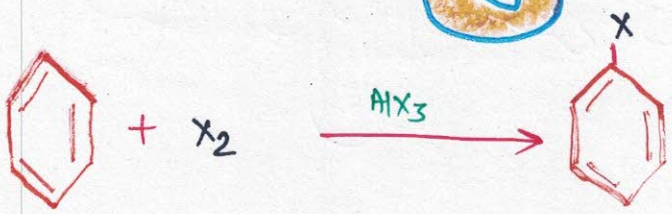
→ N will give and O won't, so phenol is still activated.





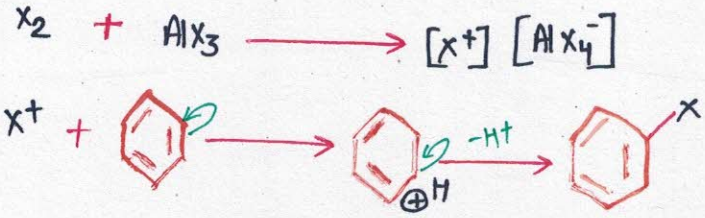
Grattermann Koch & Grattermann Synthesis never occurs at ortho or meta position.

Halogenation



It is an electrophilic substitution reaction.

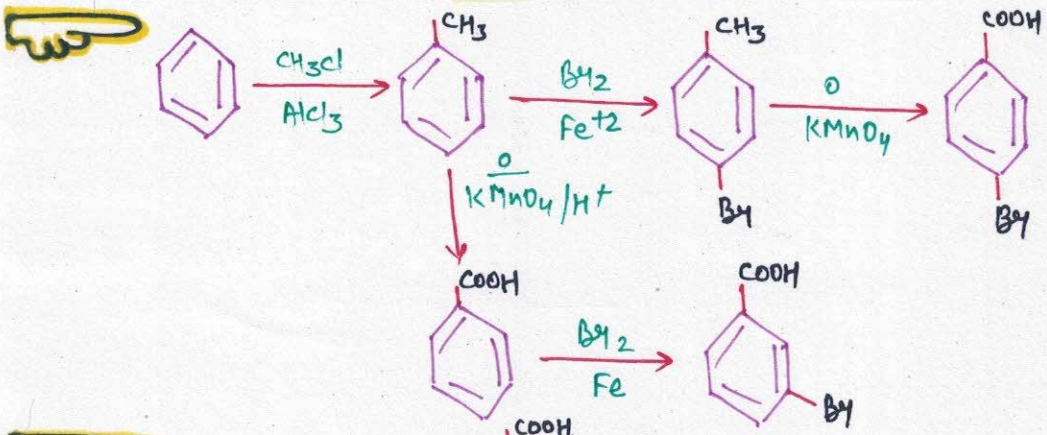
MECHANISM

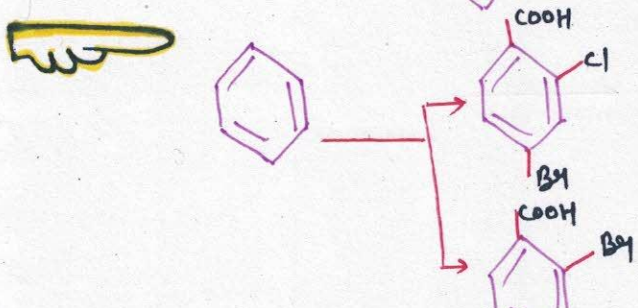


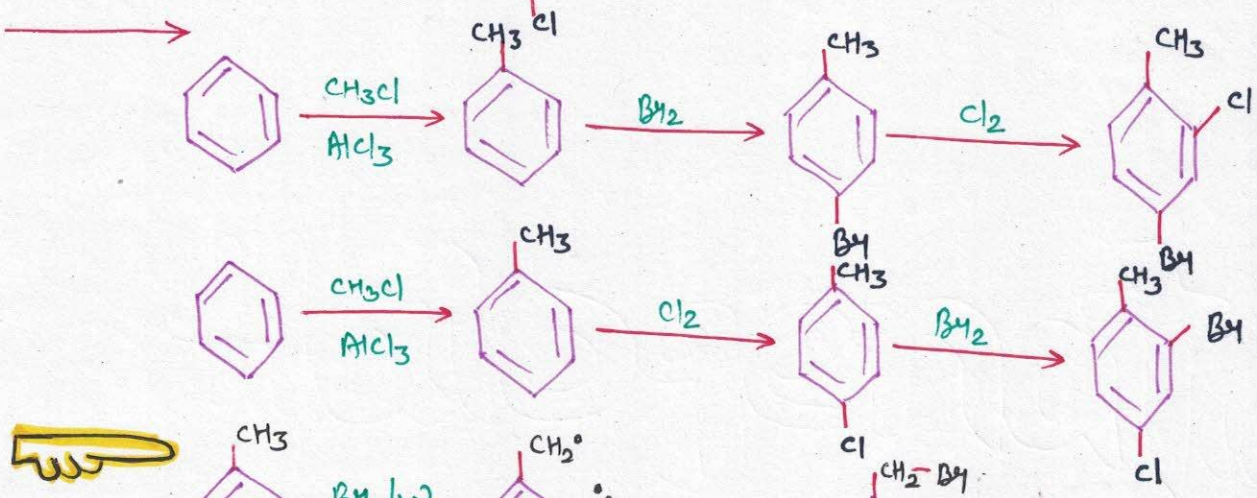
Halogenation by F_2, Cl_2 Br_2 is irreversible & I_2 is reversible.

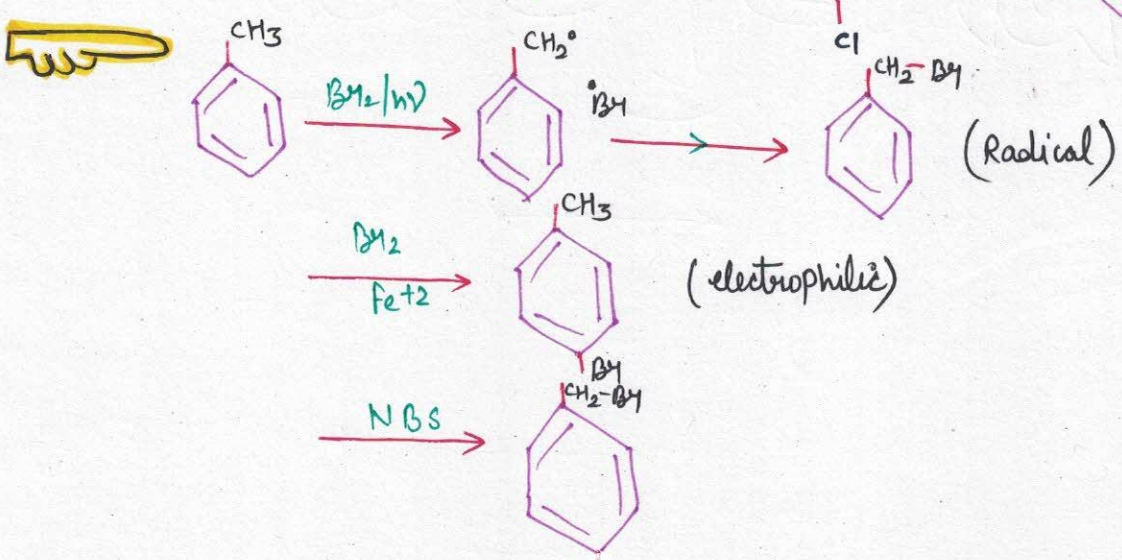
Intermediate is F^+, Cl^+, Br^+, I^+ and as for reaction to be fast intermediate should be unstable.

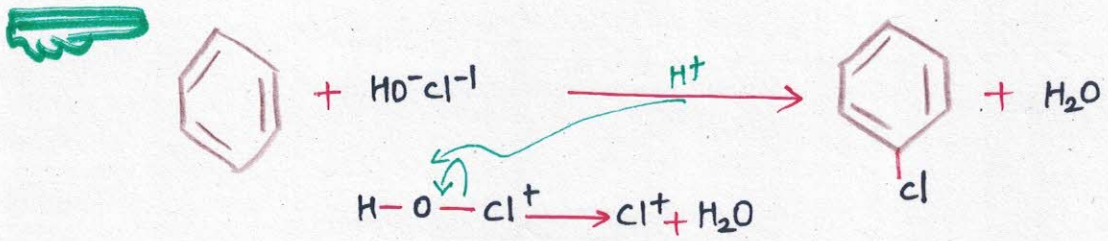
So, rate of reaction : $F_2 > Cl_2 > Br_2 > I_2$

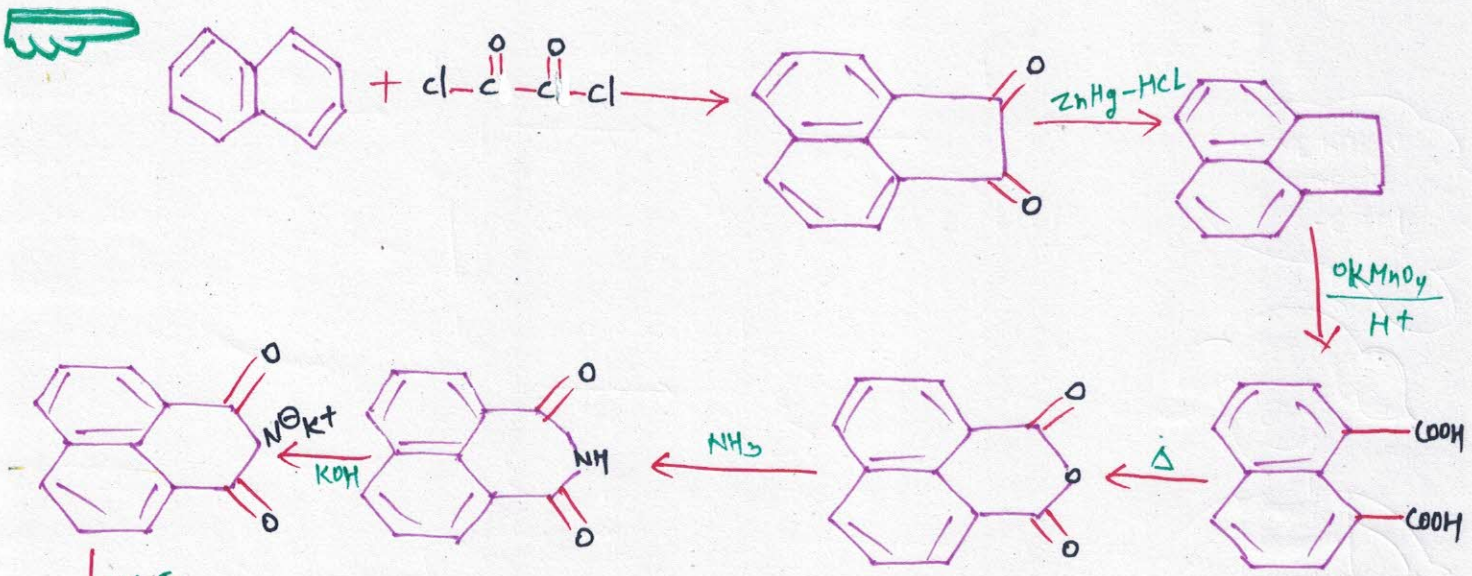


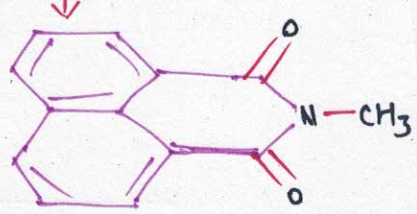




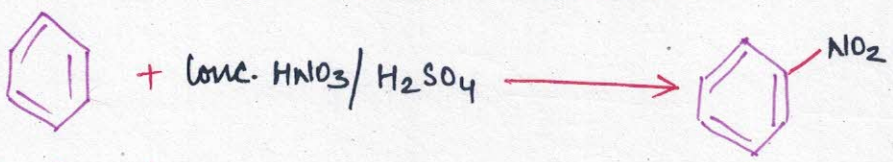




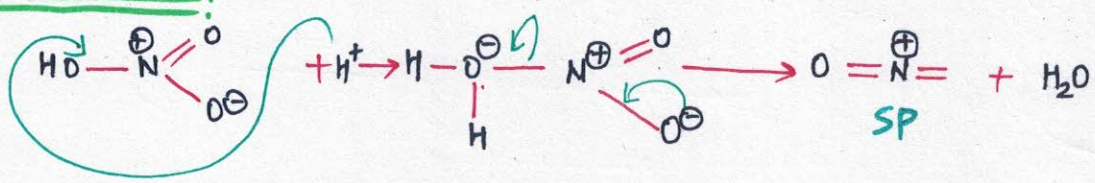


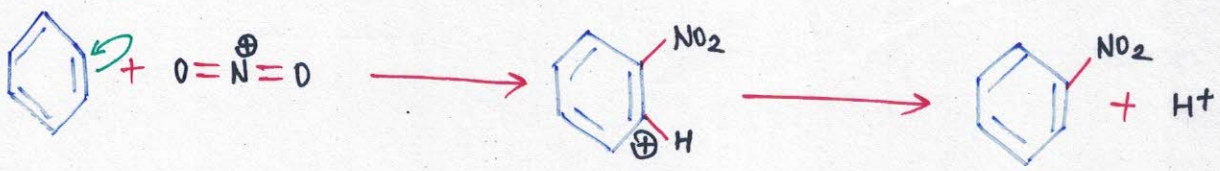


Nitration



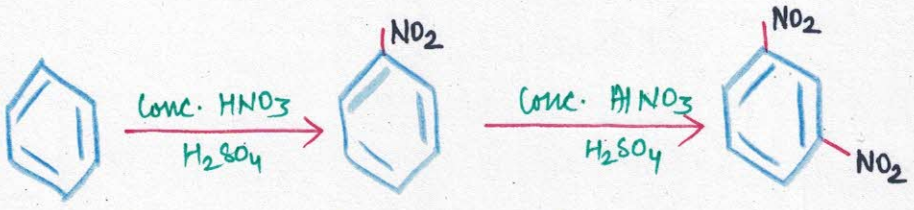
MECHANISM



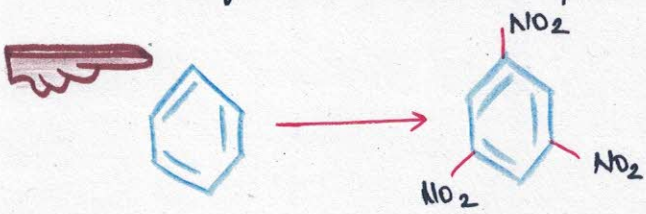


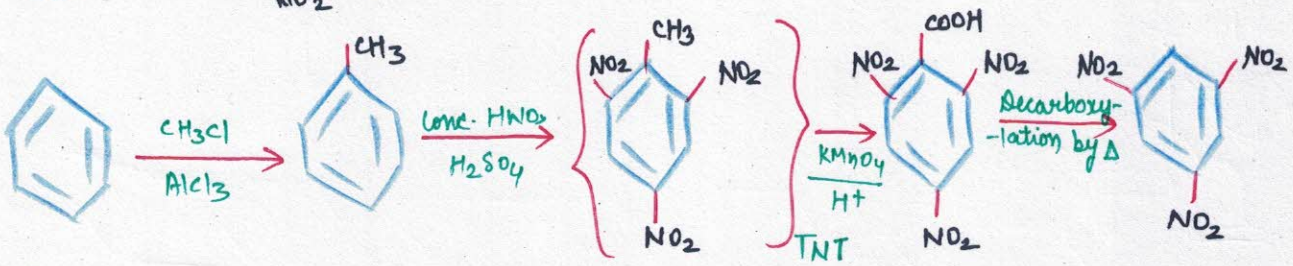
$\overset{\oplus}{N}O_2$ is isostructural with CO_2.

Nitration is irreversible.

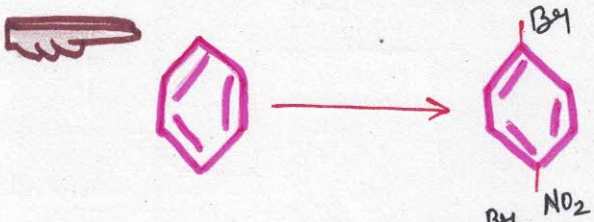


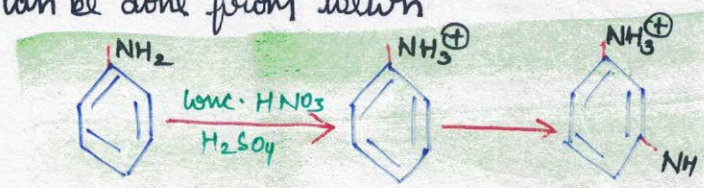
No further nitration is possible.

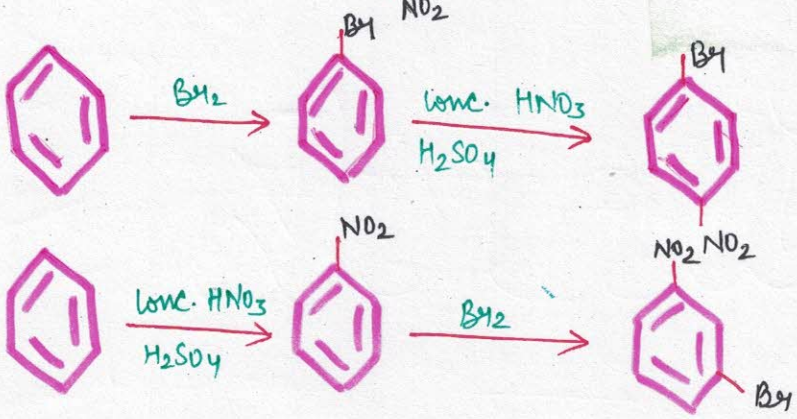


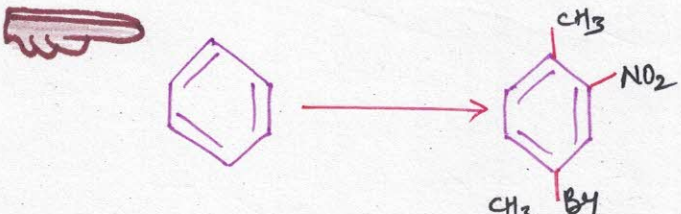


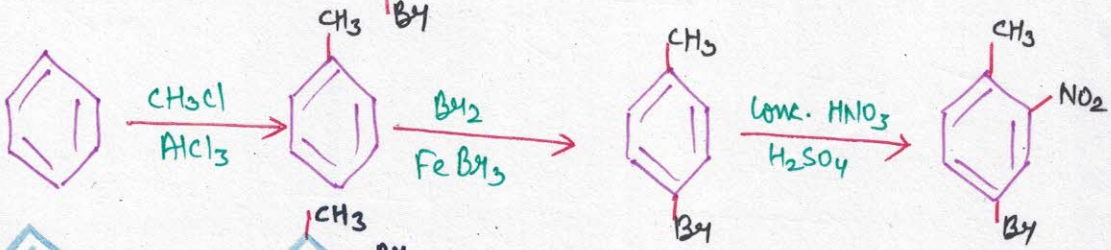
Tri nitration cannot be done on benzene but can be done from toluen

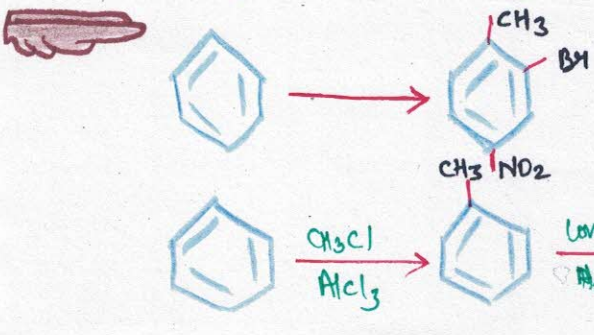




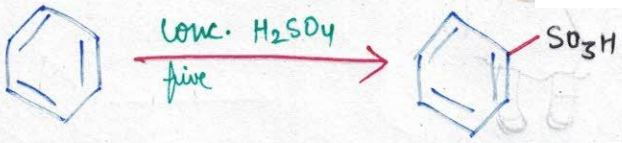






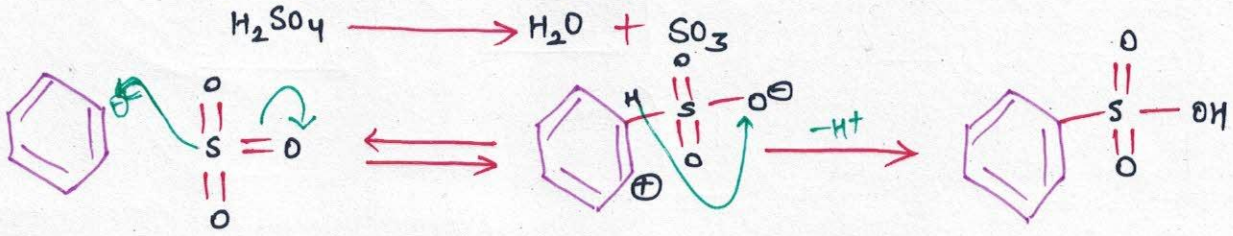


SULPHONATION

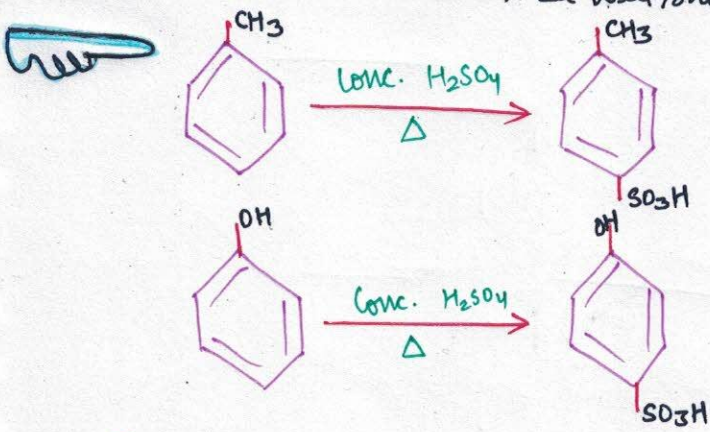


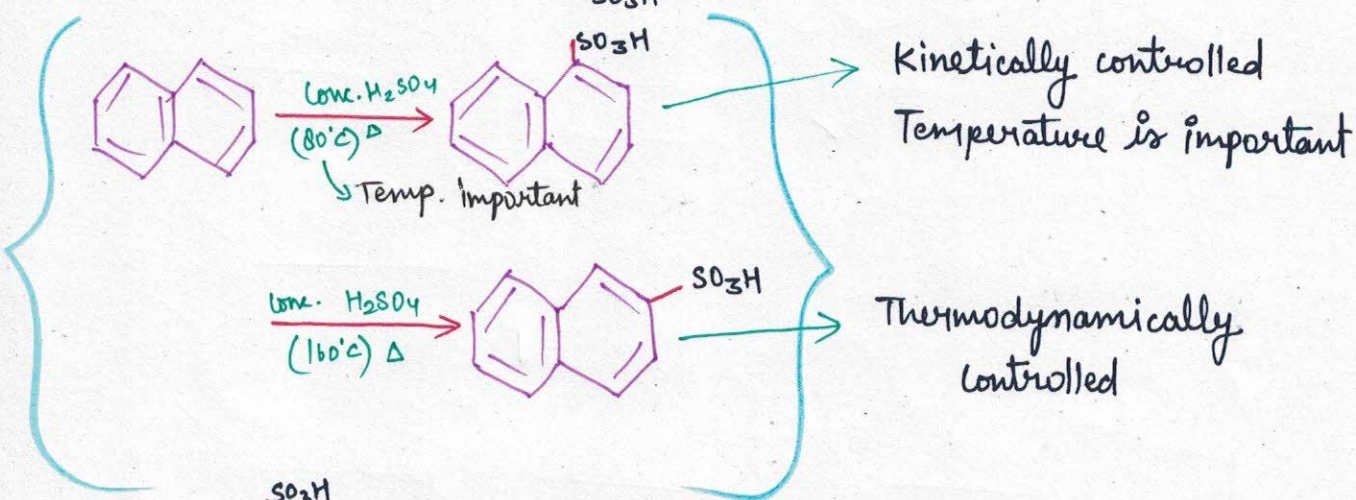
MECHANISM

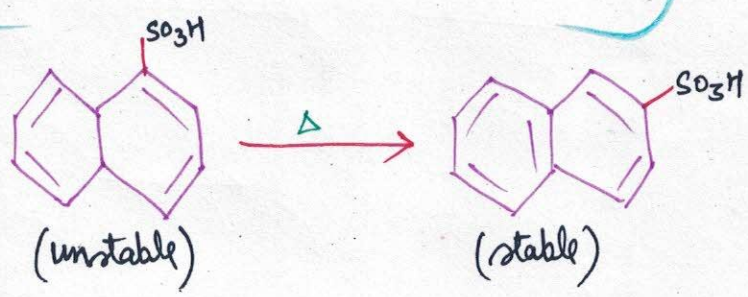
The electrophile in sulphonation is lone pair SO_3.



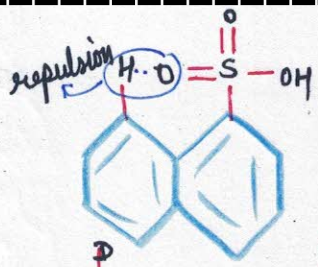
It is a reversible reaction. It will show β hydrogen isotopic effect.

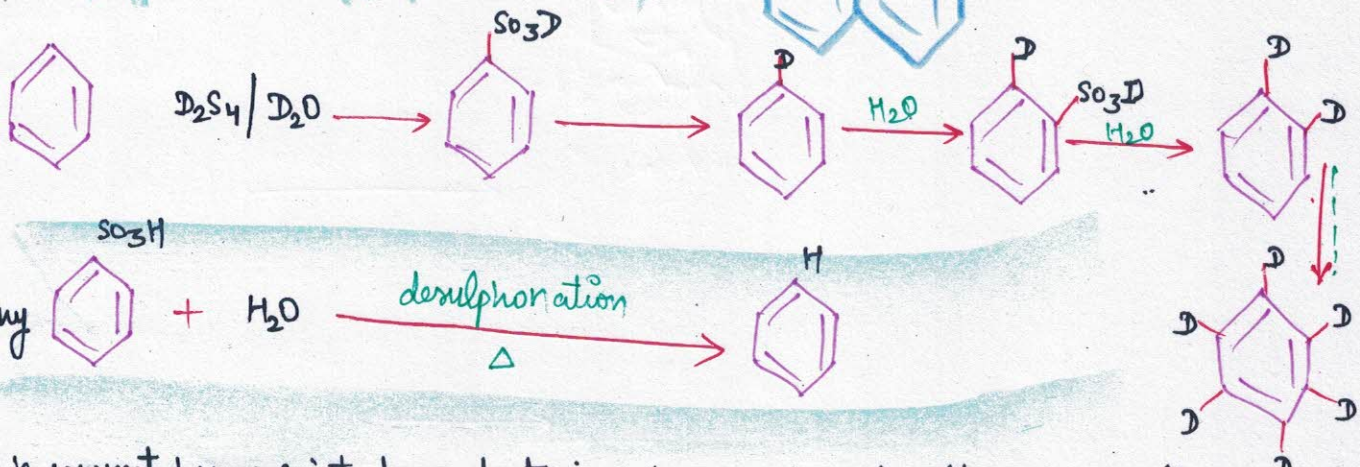




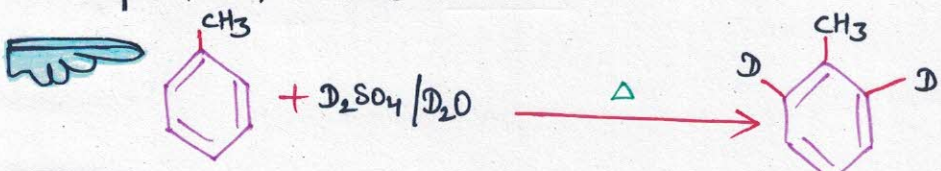


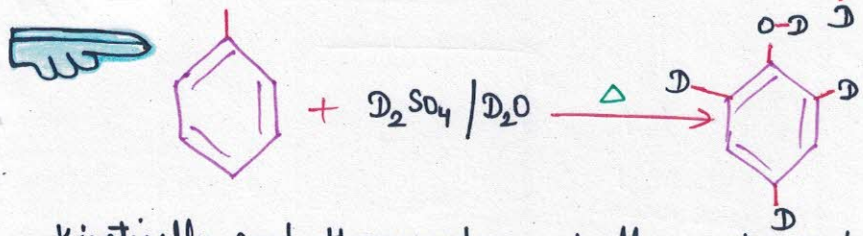
REASON OF UNSTABILITY





We convert benzene into hexa deuterium benzene by simultaneous sulphonation and desulphonation 6 times.





Kinetically and thermodynamically controlled are valid for reversible reactions only.

Test for Aromatic Hydrocarbons

1. **They are soluble in HOT conc. H_2SO_4**

Alkens are insoluble in conc. H_2SO_4 but alkens alkynes, aromatic are soluble.

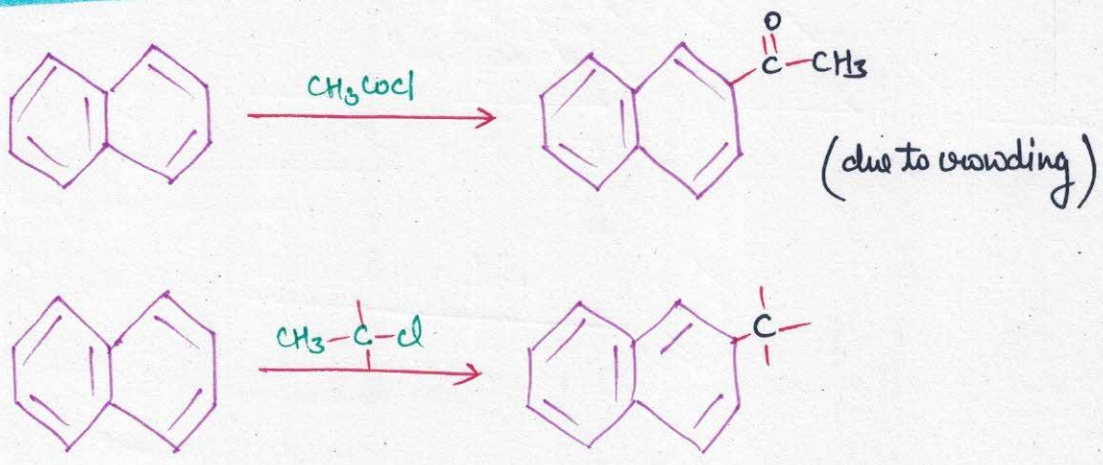
Saturated → insoluble → unsaturated → soluble

2. **They burn with sooty flame**

Difference Aliphatic do not dissolve in H_2SO_4 and burn with no sooty flame but

aromatic show both these properties

EXCEPTION



(due to crowding)