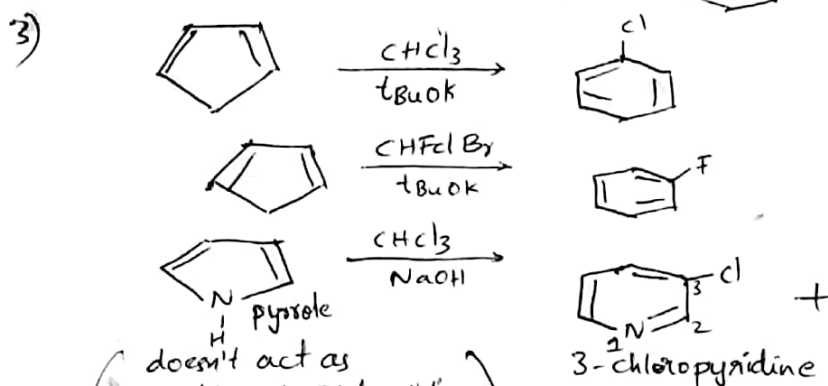
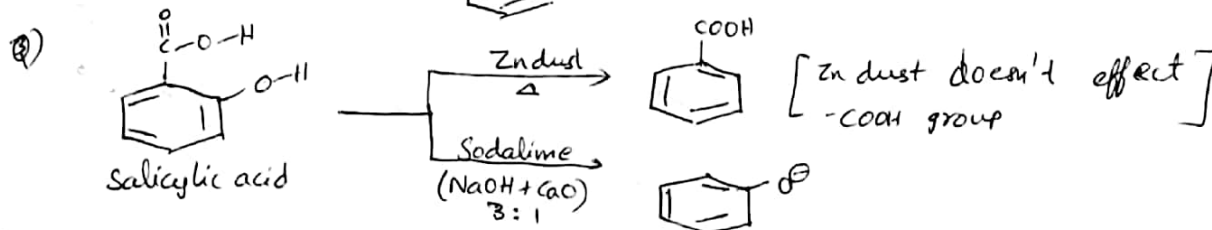
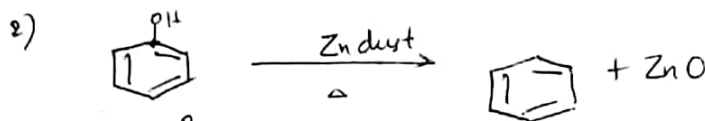
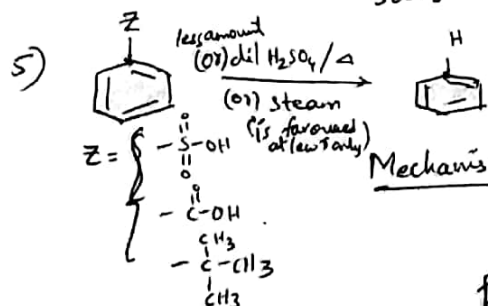
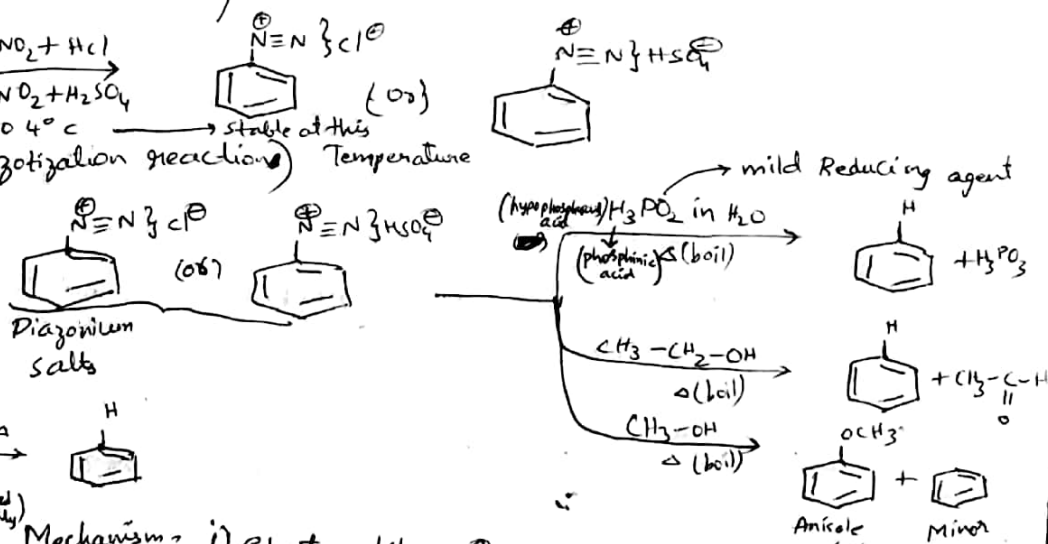
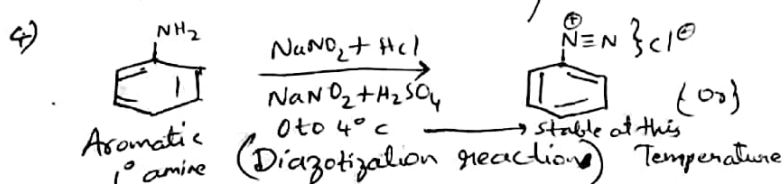
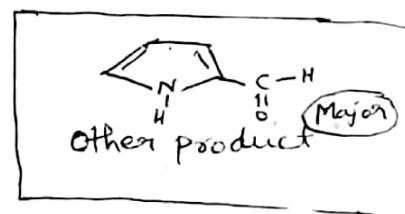


# Benzene

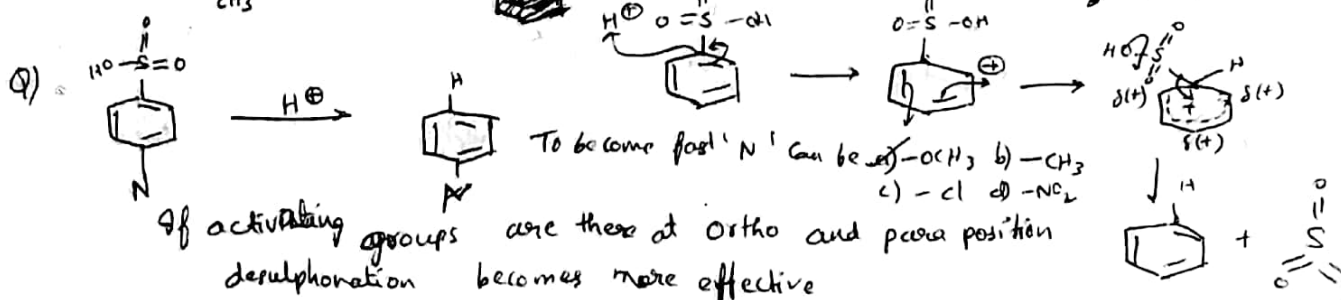
## 1) Preparation of Benzene:



doesn't act as a diene in Diels-Alder reactions but undergoes carbene addition reactions

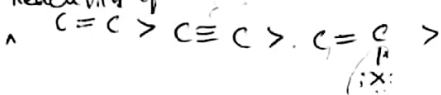


Mechanism: i) Electrophile -  $\text{H}^+$   
 ii) Attacks at IPso position (mono substituted position on Benzene is called IPso)

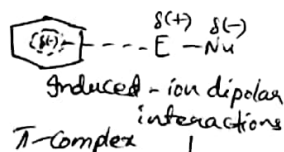
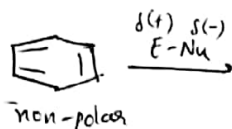


# Properties of Benzene:

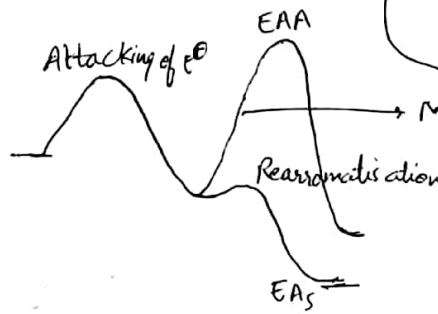
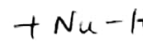
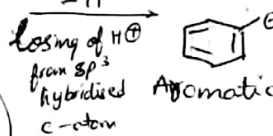
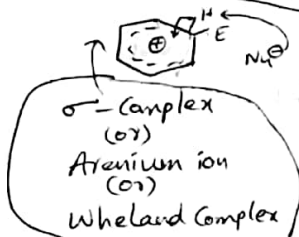
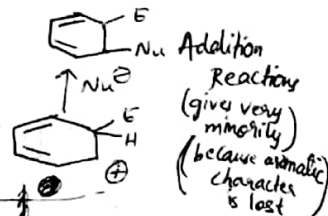
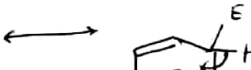
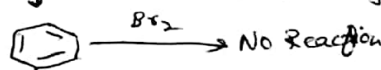
Towards  $E^+$ : Reactivity of



(Due to Aromatic behaviour the  $\pi$ -e's in benzene are held relatively strongly)

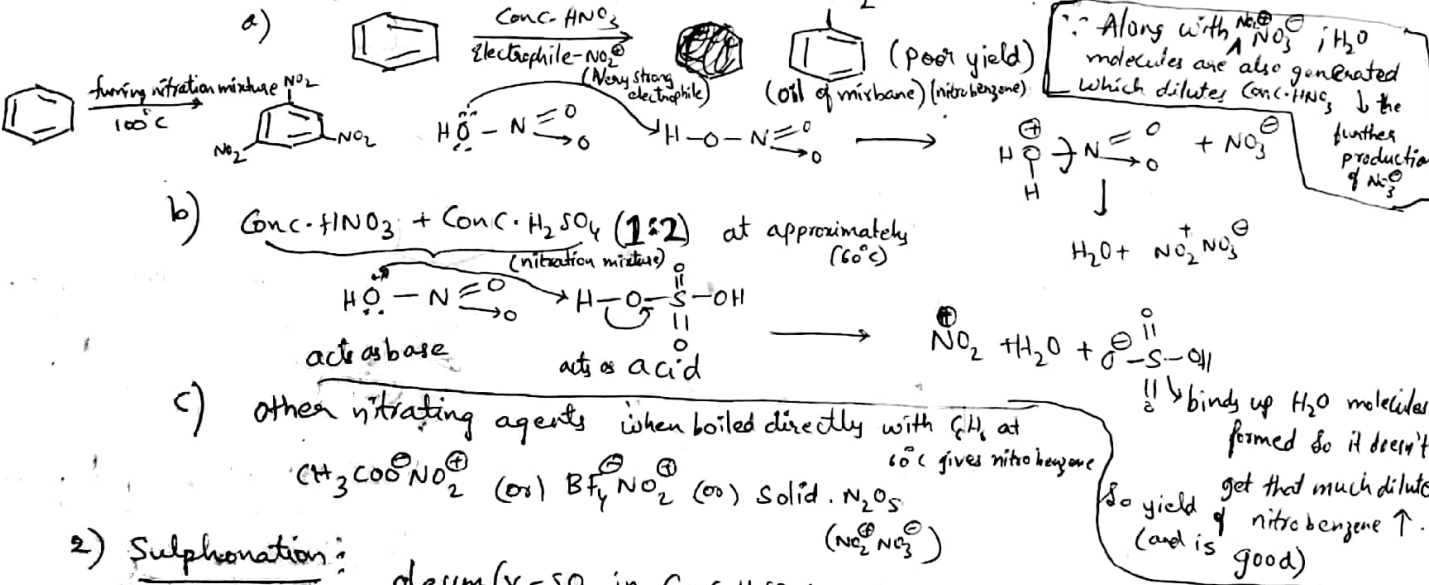


If Electrophile has sufficient amount of  $\Delta V$  charge then

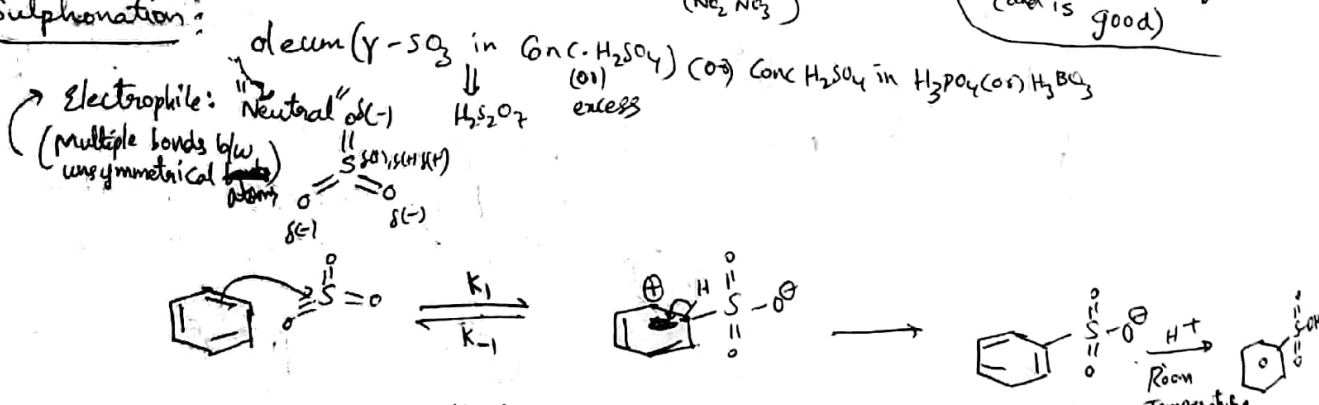


Most of the aromatic compound won't choose this path i.e., don't undergo (or) undergoes very less electrophilic addition reaction. But most of them undergo Electrophilic Substitution reactions.

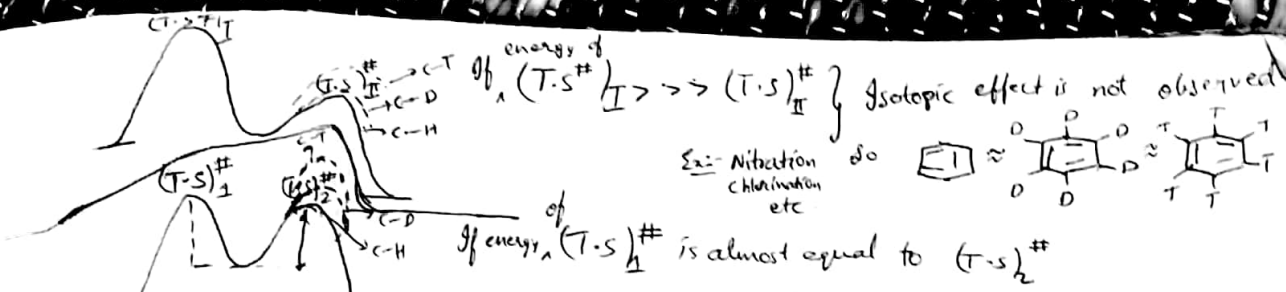
## 1) Nitration



## 2) Sulphonation:



Note: 1) For all EAS reactions; attacking of electrophile is slow step (step 1)



The energy barriers on either side of  $\sigma$  formed are of equal height  $\Rightarrow$  same molecules go to products and different back to starting material

So in case of Sulphonation (or)

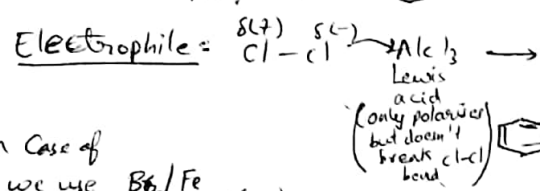
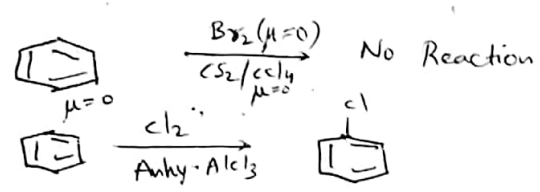
Iodination (or) Nitrososation

On deuterated benzene or tritiated benzene the rate determining step is second-step i.e., not the attack of electrophile but in case of Nitration, Iodination, Nitrososation, done on Benzene ring will have R.D.S. step as step-I only i.e., electrophile attack

Ex: Sulphonation (In case of this reaction the barrier will be second graph drawn as above)  
Iodination  
Nitrososation (Nitrosonium ion)

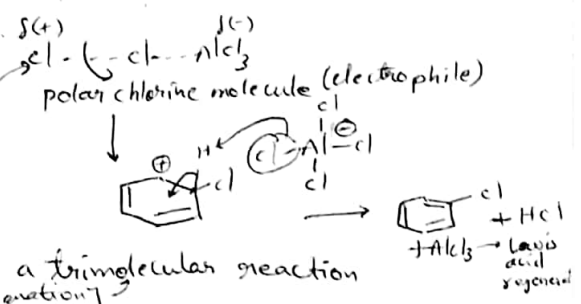
Low electrophile  
Leaving group ability  
There is a greater chance (or) almost equal chance for both  $H^+$  & electrophile to leave the benzene system which can be concluded from the energy barriers in second graph so that's why reactions are reversible

### Halogenation:

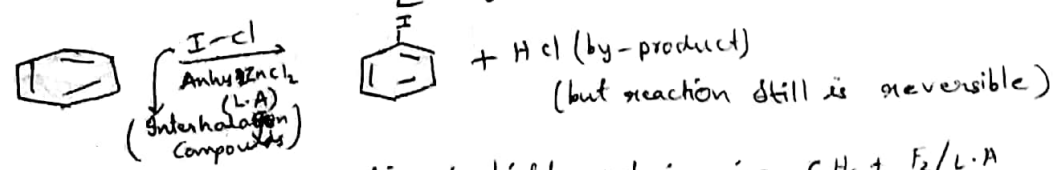
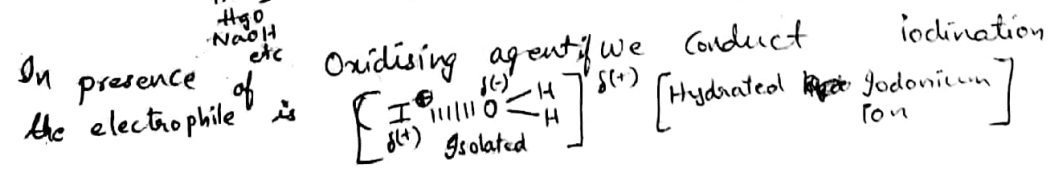
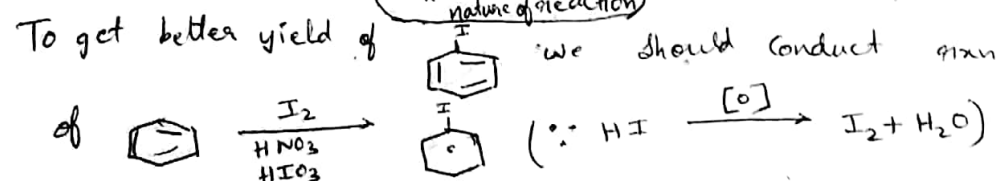


### Bromination

Similarly in case of bromination we use  $\text{Br}_2/\text{Fe}$  (Scrap iron)  
 (or)  $\text{Br}_2/\text{FeBr}_3$  (or)  $\text{Br}_2/\text{AlCl}_3$   
 (hygroscopic; so Scrap iron is used along with  $\text{Br}_2$  doesn't polarise effectively)

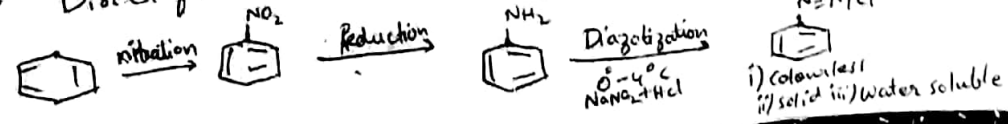


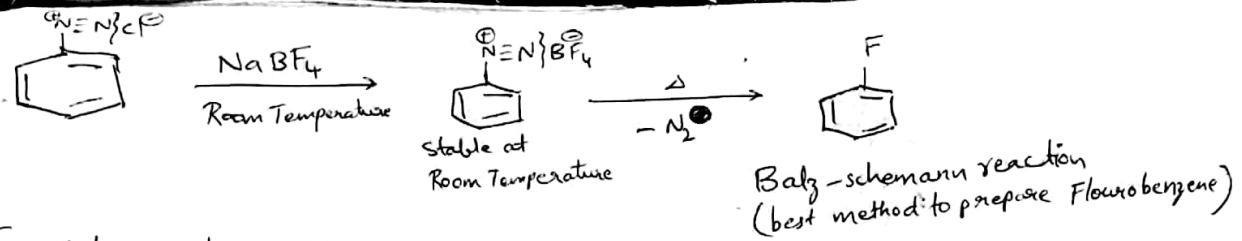
### Iodination



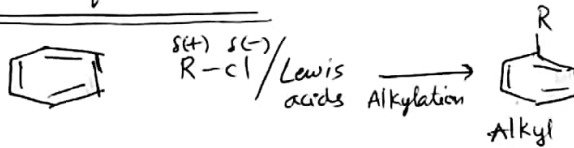
### Fluorination:

Direct fluorination is highly explosive i.e.,  $\text{C}_6\text{H}_6 + \text{F}_2/\text{L.A.}$





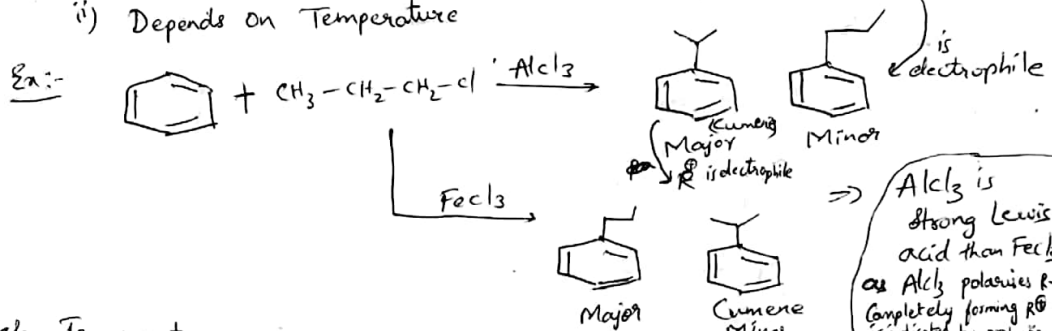
### Friedel-Crafts Reaction:



\* Generally nitrobenzene is used as solvent in Friedel crafts rxn.

Mechanism: Electrophile may be  $R^+$  (or)  $R^{\delta(+)}-Cl^{\delta(-)}-L.A.$  it depends on polarized Alkyl halide

i) strength of the Lewis acid and nature of  $R-X$   
 ii) Depends on Temperature

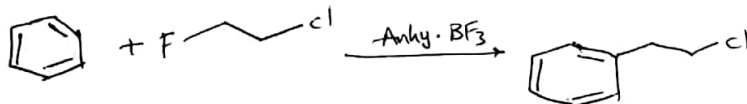


$\Rightarrow$   $AlCl_3$  is strong Lewis acid than  $FeCl_3$   
 as  $AlCl_3$  polarizes  $R-X$  completely forming  $R^+$  which is indicated by production of this  $R^+$  product as major one

Note:- At high Temperature, Rearrangement is most common in presence of any Lewis acid  $\Rightarrow$  Rearranged product is major.

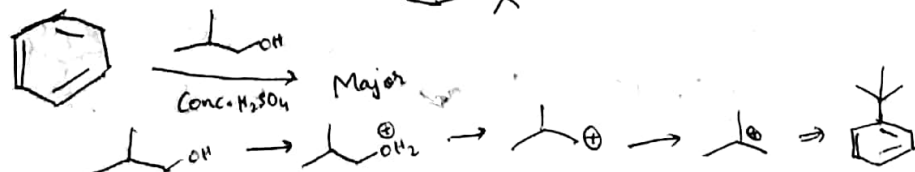
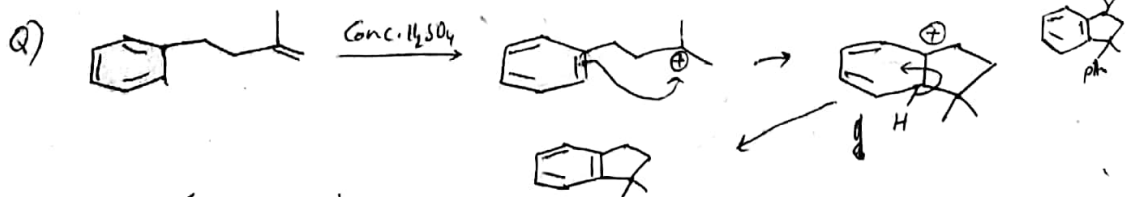
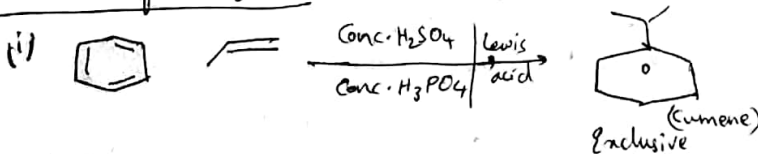


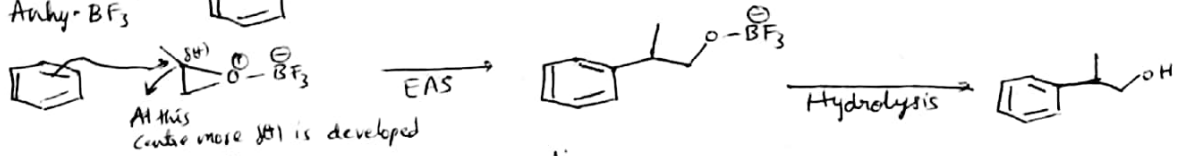
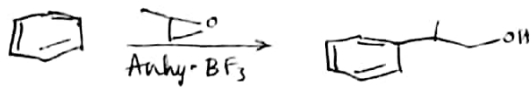
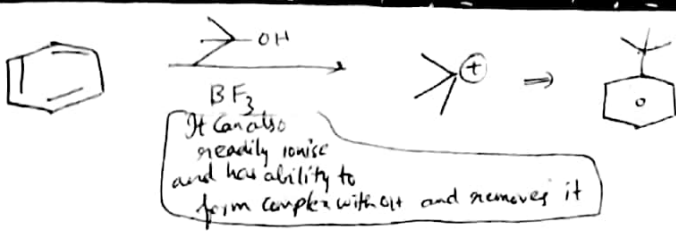
No Reaction  $\left( \begin{array}{l} \because i) BF_3 \text{ is a weak Lewis acid} \\ ii) BCl_3 \text{ doesn't polarize } R-X \\ \because BCl_3^- \text{ doesn't exist} \end{array} \right)$



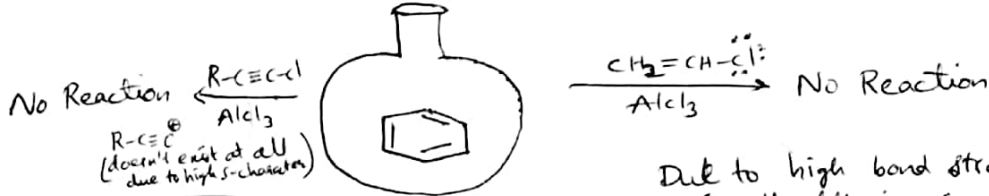
$\therefore$  polarisability of  $-F > -Cl > -Br > -I$  (not based on bond strength)  
 So reactivity of  $\uparrow$

### Other methods for Alkylation





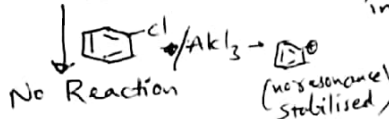
Predict the products for the following reactions



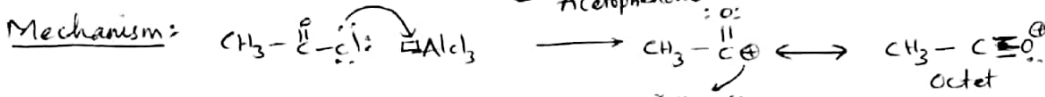
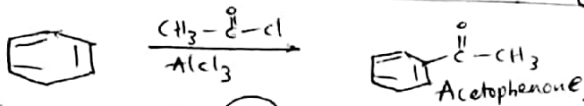
$\text{R}-\text{C}\equiv\text{C}^+$   
 (doesn't exist at all due to high s-character)

Due to high bond strength of C-Cl in the following compounds and due to instability of  $\sigma^+$  formed after losing Cl so reaction doesn't take place.

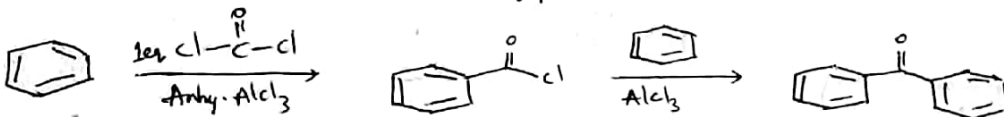
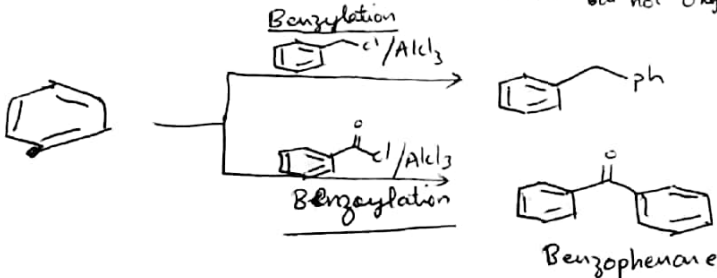
So alkynyl halides and alkynyl halides do not act as alkylating agents



Friedel Crafts Acylation / Friedel Crafts Acetylation reaction:

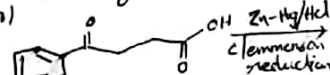
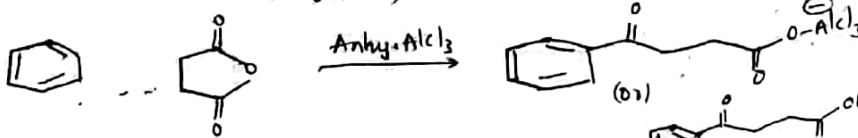
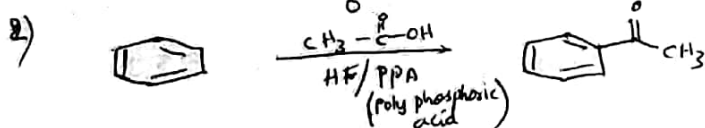
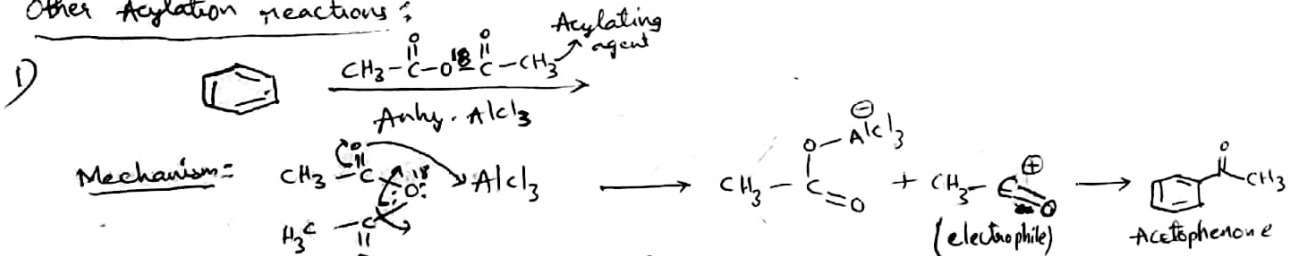


Benzene attacks carbon but not oxygen ( $\because$  charge present on Oxygen is not a real charge)

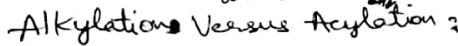


1 eq. of phosgene reacts with 2 eq. of Benzene

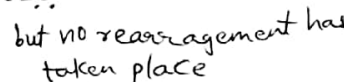
Other Acylation reactions:



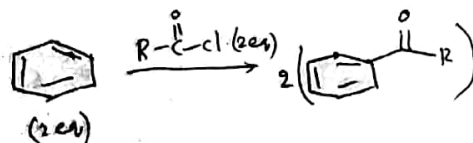
Generally pure metals or metals dipped in some solvents do not mediate carbonylic acids but only reduce carbonyl compounds



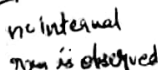
with anisole gives acylated product

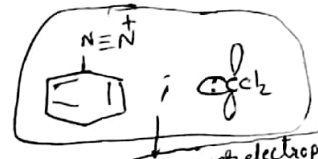
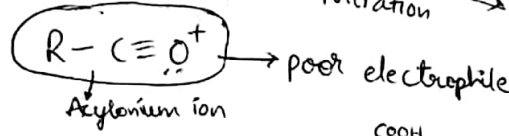
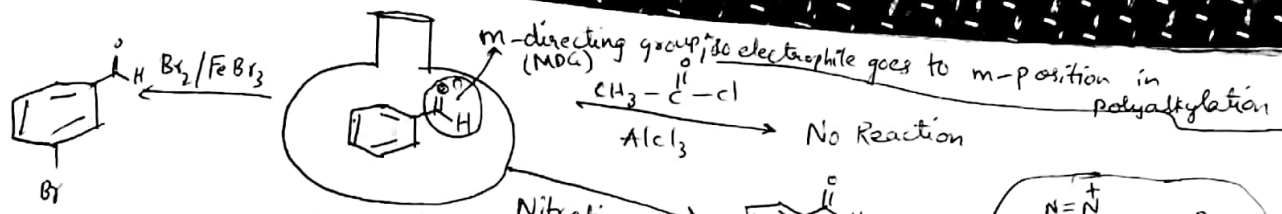
[illegible]

(Thermodynamically stable product is formed at high T)

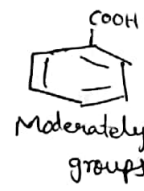
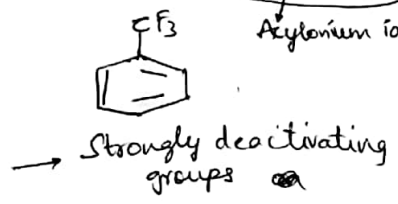


∴ Reactivity of Substrate is Greater than the product formed so again reactant only will react with excess of reagent to give <sup>some</sup> product.





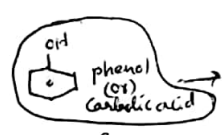
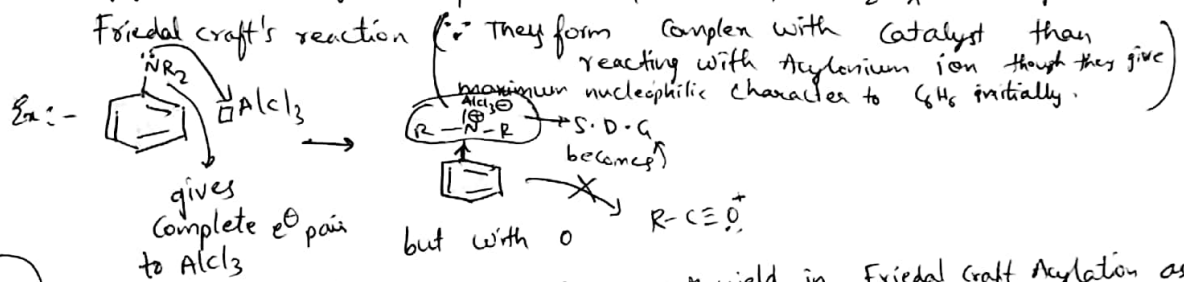
Very poor electrophiles that they do not react with Benzene and only react with strong activating benzene substituents groups like  $-O^-$ ,  $-NH_2$



doesn't give Friedel Craft Acylation reactions

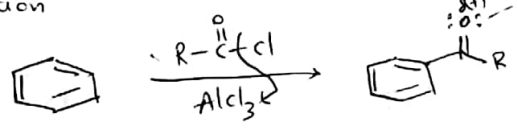
Weakly deactivating, Weakly activating, Moderately activating groups on Benzene ring gives Friedel Craft Acylation reactions

Strongly activating groups ;  $-NR_2$ ,  $-NH-R$ ,  $-NH_2$  also doesn't give Friedel craft's reaction



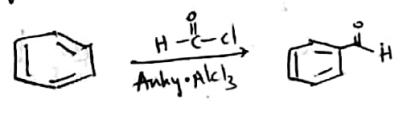
Strongly activating OH group gives poor yield in Friedel Craft Acylation as it doesn't form complex that effectively and almost maintains equal connections with Benzene and also with Catalyst

Excess of Catalyst is required in case of Acylation which is not needed in case of Alkylation



Unwarrantedly  $AlCl_3$  will form complexes so take add excess of catalyst so that to  $\uparrow$  yield

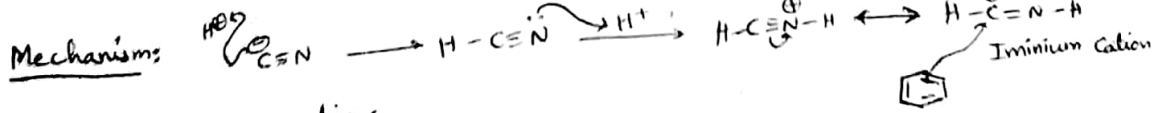
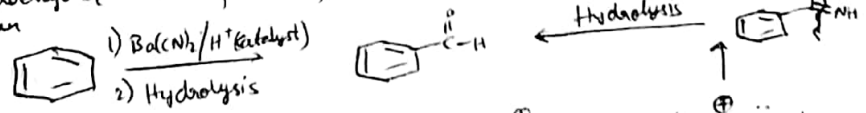
Note:- Friedel craft's failed to synthesize formaldehyde from formyl chloride ( $\because$  It doesn't exist at experimental conditions)



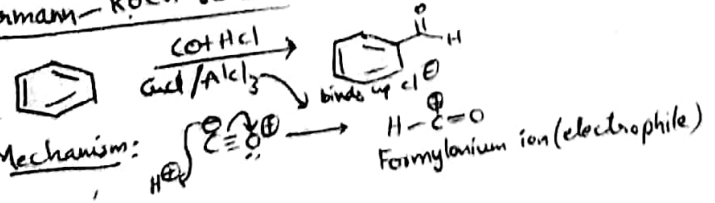
At above this T it decomposes as  $CO + HCl$

To prepare Benzaldehyde, other proposed reactions are

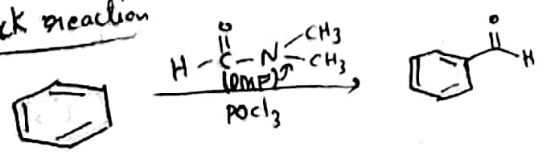
1) Gattermann's

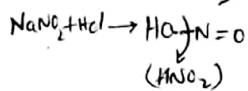
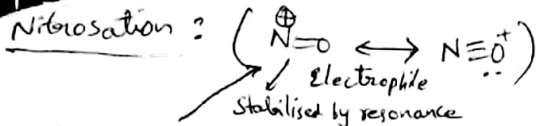


2) Gattermann-Koch reaction

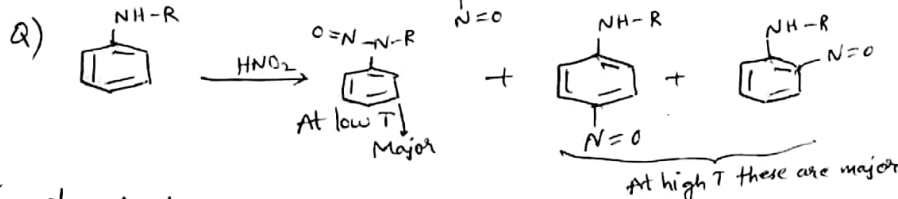
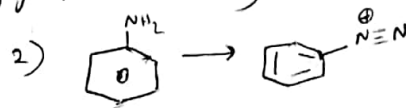
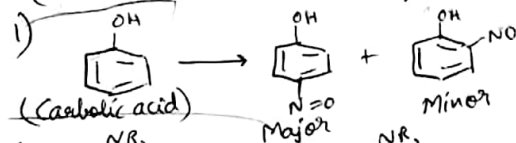


3) Vilmeier Haack reaction





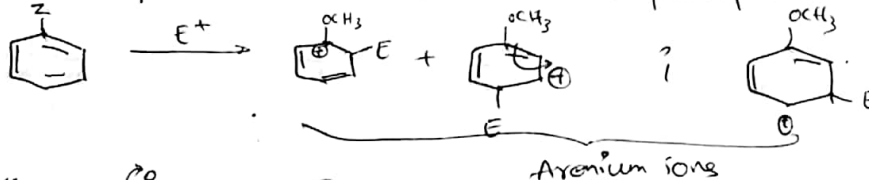
(It reacts with all strongly activating groups on Benzene)



Orientation of electrophile in mono substituted Benzene:

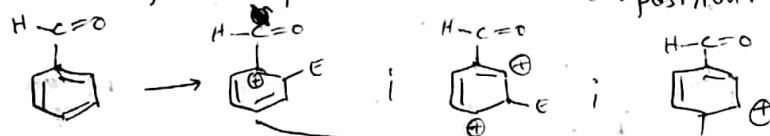
Case (i) : Z :-  $-\text{OCH}_3$ ,  $-\text{NH}_2$ ,  $-\text{O}-\text{C}(=\text{O})-\text{R}$ ,  $-\text{S}(=\text{O})_2-\text{R}$ ,  $-\text{CH}=\text{CH}_2$ ,  $-\text{Ph}$ ,  $-\text{X}$  (where X is halogen)  $\rightarrow$  +M, deactivating groups, but o,p directing groups

During reaction, the intermediate stability decides the attacking of electrophile. So in the presence of these groups on benzene group Electrophile is more stable at ortho and para positions.



Case (ii) :-  $-\text{C}(=\text{O})\text{H}$ ,  $-\text{N} \equiv \text{O}$  etc

-M-directing doesn't  $\uparrow$   $e^-$  density at meta position but they decrease  $e^-$  density more at ortho and para position so relatively electrophile attacks at meta position.



Case (iii) :-  $-\text{CH}_3$ ,  $-\text{Et}$ ,  $i\text{-Pr}$   $\rightarrow$  behaves like +M due to hyperconjugation. Arenium ion stability is important.

So Electrophile attacks relatively at ortho and para positions

Case (iv) :-  $\rightarrow$  o and p  $>$  m  $\rightarrow$  based on stability of Arenium ion

Case (v) :-  $-\text{CF}_3$  and  $-\text{CCl}_3$   $\rightarrow$  meta directing  $m >$  o and p  $\rightarrow$  based on stability of Arenium ion

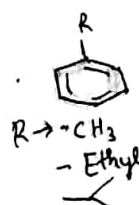
Case (vi) :- Z  $\rightarrow$  neither +M nor -M

Ex:-  $-\text{NH}_3^+$ ,  $-\text{NR}_3^+$  (only -I)

Meta is better than ortho and para based on stability of Arenium ion

% of ortho vs para:

1) Size of the group



Nitration  $\rightarrow$

	Ortho	para	meta
$-\text{CH}_3$	58%	37%	5%
$-\text{Ethyl}$	45%	49%	6%
	30%	62%	8%



## 2) Size of electrophile



EAS

Chlorination  
Nitration  
Sulphuration  
Bromination

16%  
73%  
11%

O

P

39

55

30

69

1

99

11

87

## 3) Electronegativity of substrate



Nitration

-F  
-Cl  
-Br  
-I

O

P

12

88

30

69

32

62

28

60

## 4) Reactivity towards EAS

i)



ii)



iii)



iv)

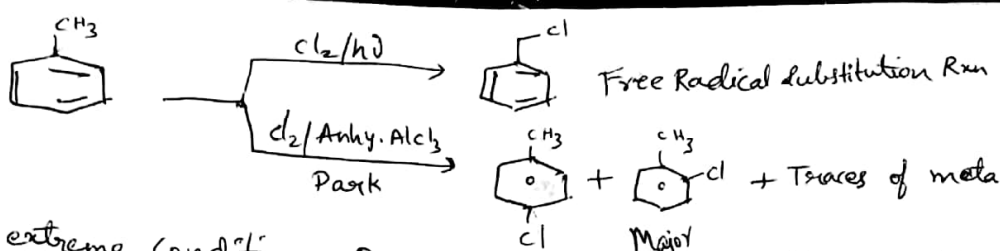


Which of them are m-directing predominantly -6

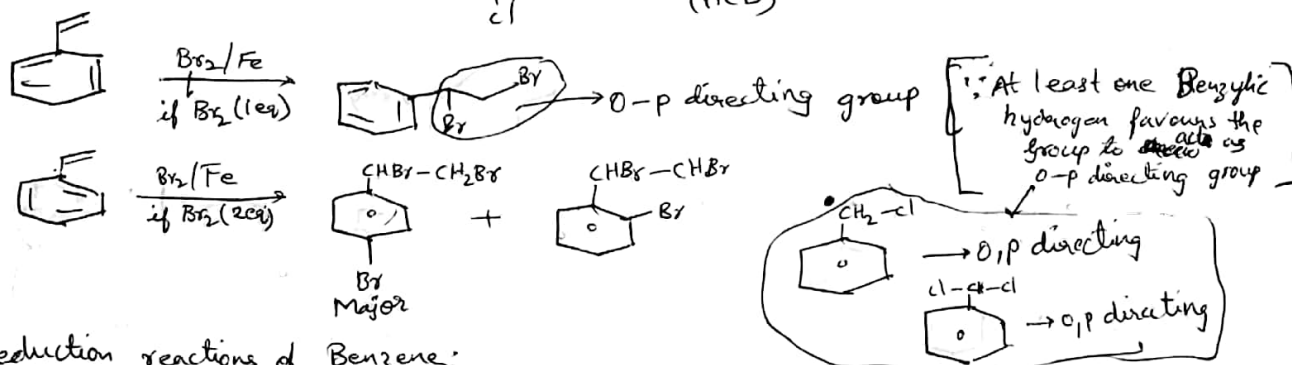
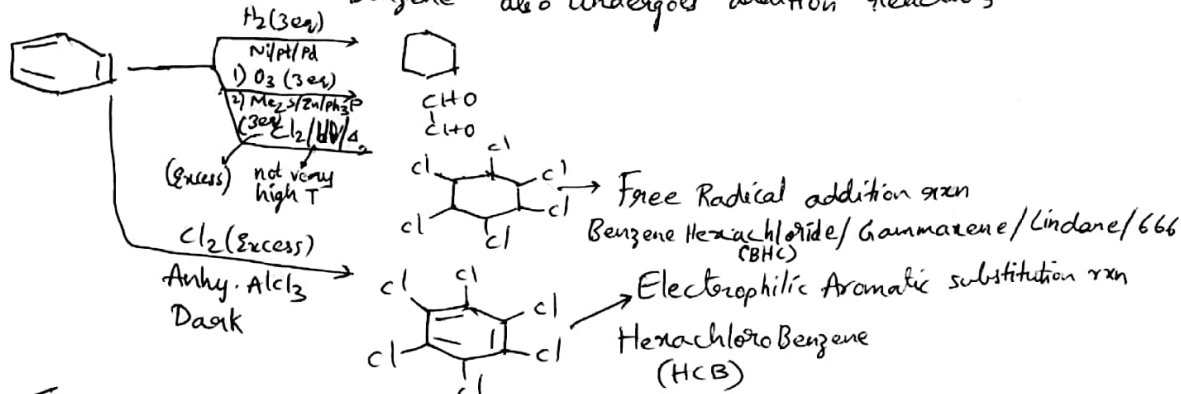
1)



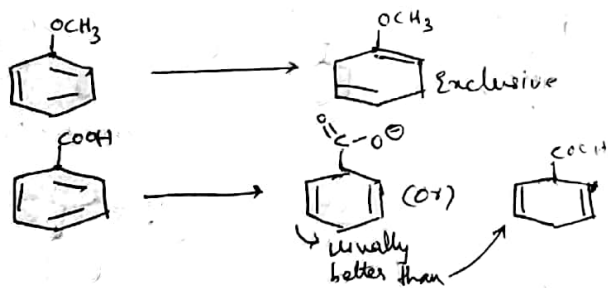
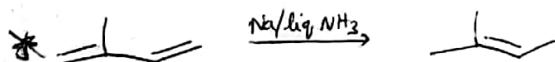
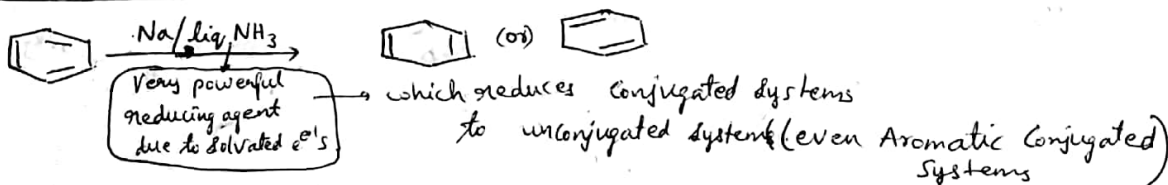
Q)



Under extreme conditions Benzene also undergoes addition reactions

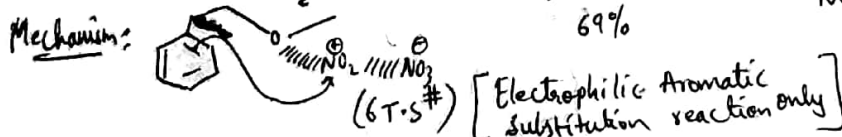
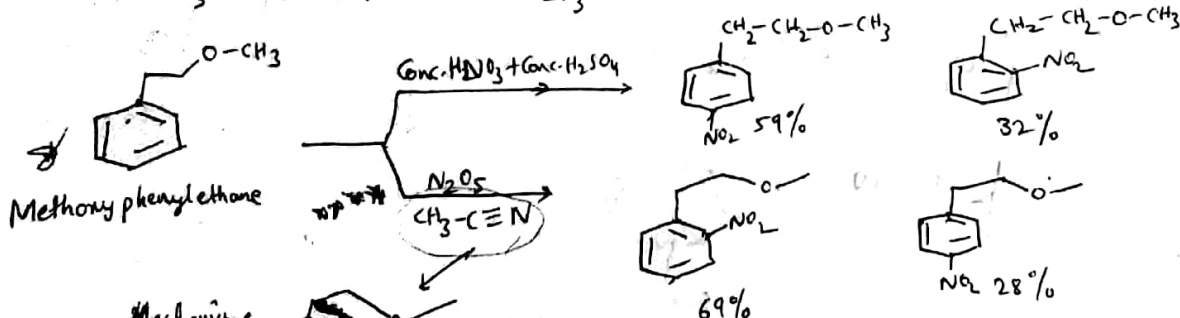
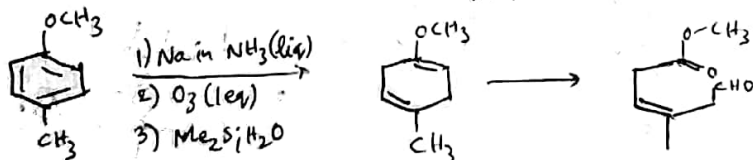


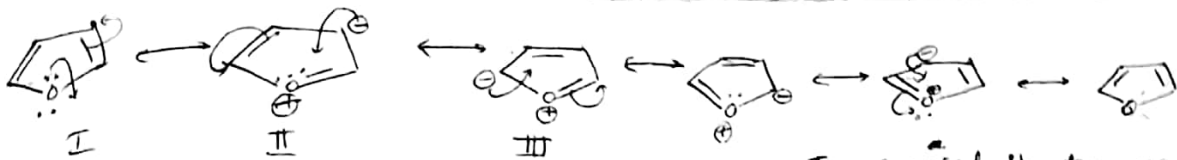
Reduction reactions of Benzene:



If Activating groups are present: the product is  $\pi$ -bond at IPSO position

If Deactivating groups are present the product is  $\pi$ -bond w/o at IPSO position



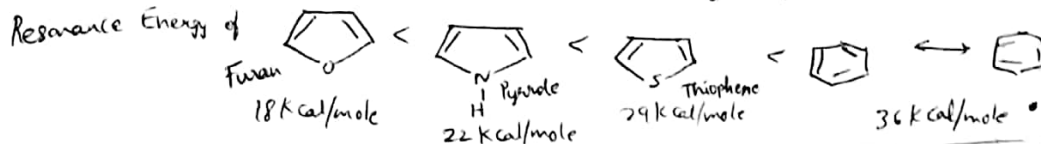


Stability of  $I > III > II$

Five canonical structures are possible for furan



8 Canonical structures are possible for Thiophene



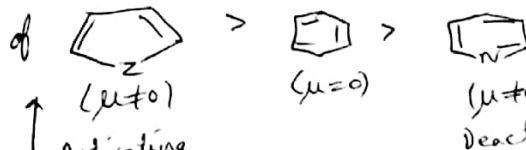
Though only 2 resonance structures are there for benzene but it has high R.E. due to delocalisation of  $\pi$  electrons.

R.E. of Pyridine is 29 kcal/mole

No. of R.E's  $\rightarrow$  Pyridine

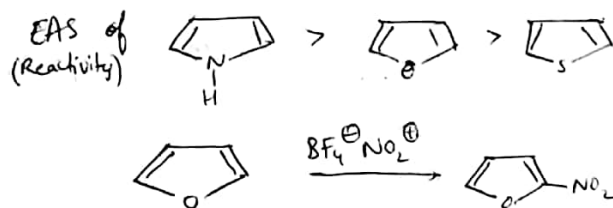
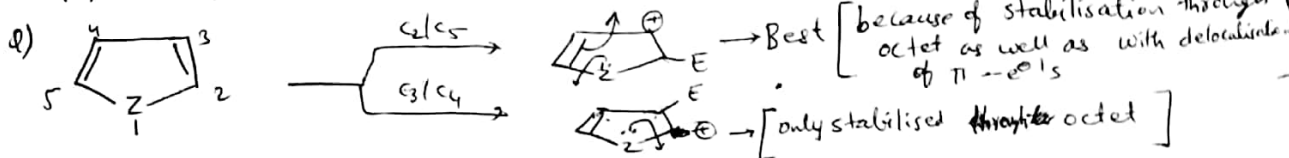
It can show both types i.e., delocalisation of  $\pi$  electrons involving lone pair of nitrogen like an imine group with change separated conjugation like tropine.

Towards Electrophilic Aromatic substitution

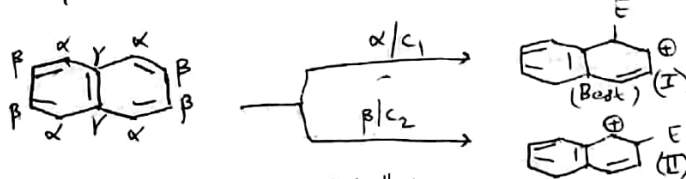
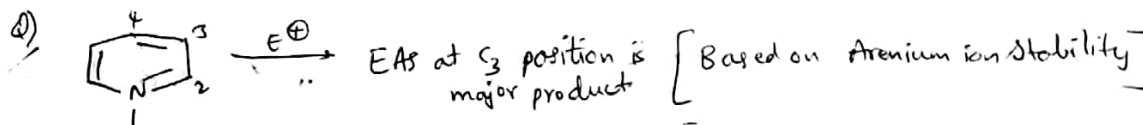


Activating

Deactivating



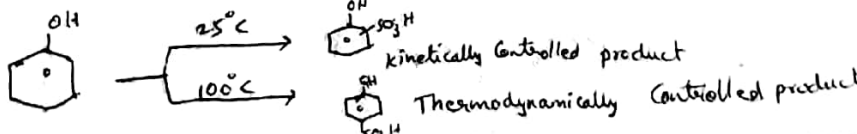
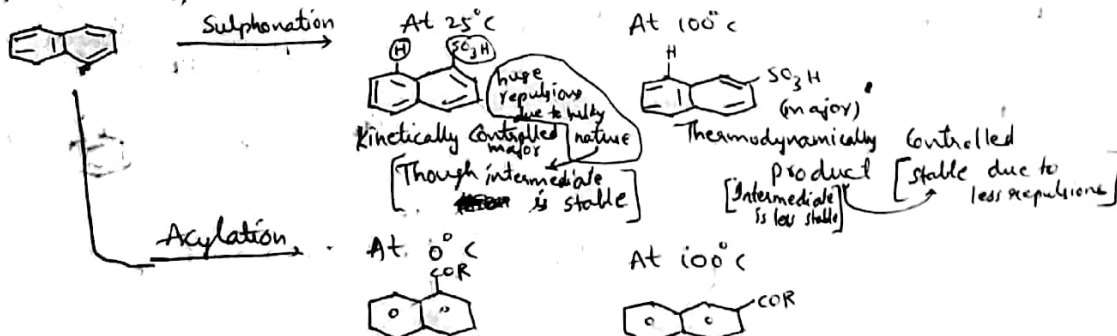
Based on Arenium ion stability. So we cannot say that if stability is more then reactivity is less (or) vice-versa. Though pyridine has high R.E. than furan, it is stable but it only has high reactivity than furan.

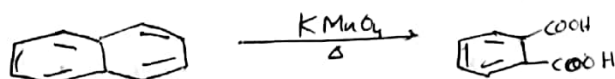


Both these structures have equal number of resonating structures but in (I) most of the canonical forms have aromatic system than in case (II).

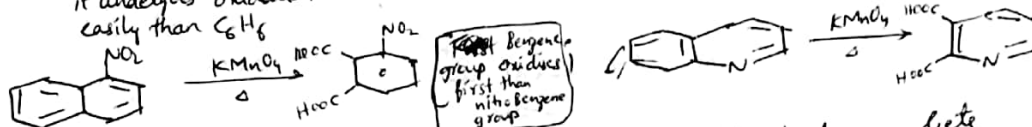
EAS reactions based on K.E. Controlled vs Thermodynamically Controlled products.

$\rightarrow$  If electrophile is bulky; Temperature variation

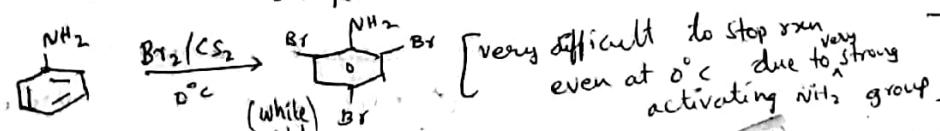
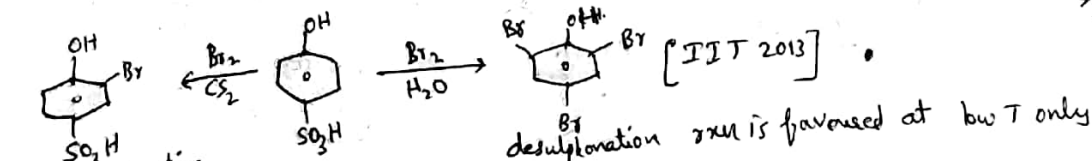
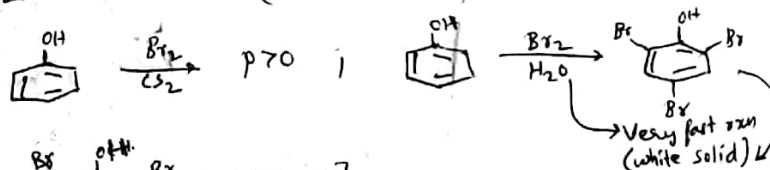
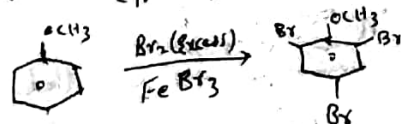
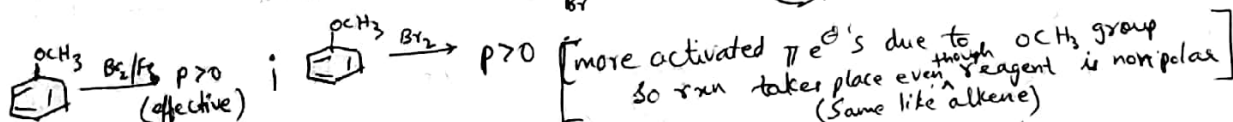
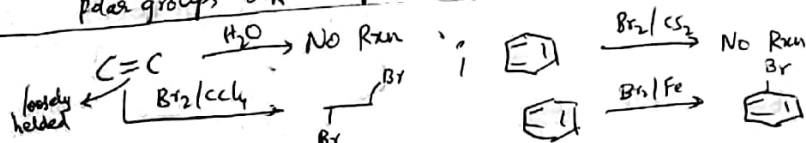
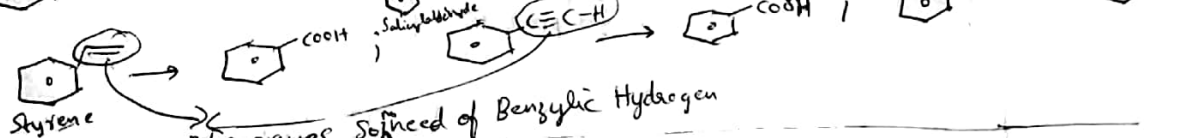
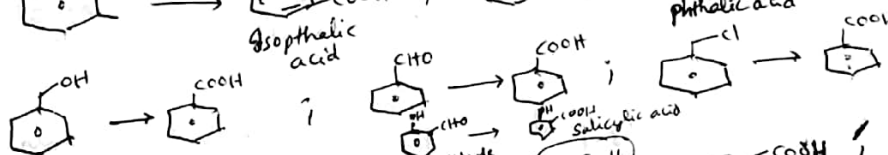
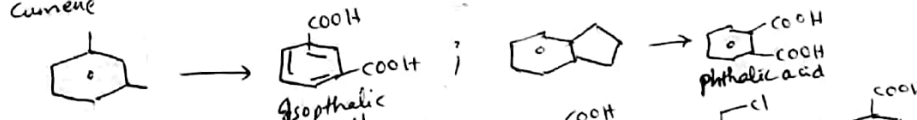
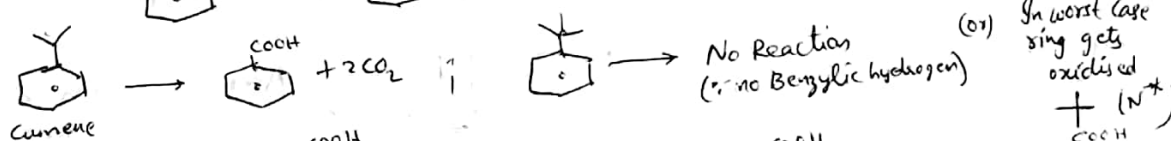
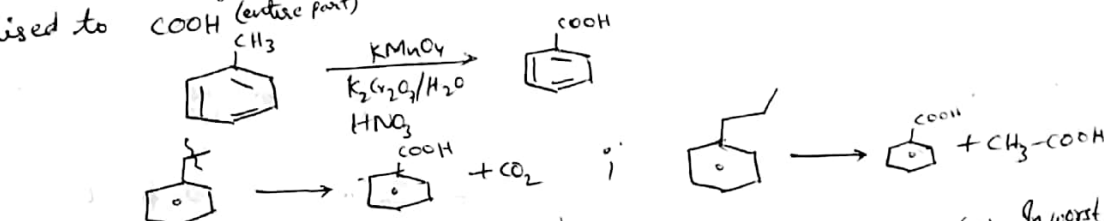




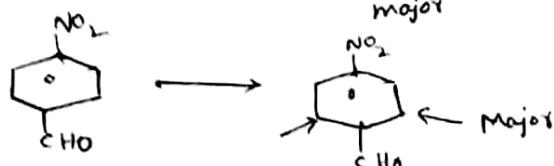
due to less R.E./ring  
it undergoes oxidation  
easily than  $C_6H_6$



Alkyl substituted Benzenes if possesses atleast one Benzylic hydrogen gets oxidised to COOH (entire part)







does not  
favour

→

Major

Minor

$CF_3$

[illegible]

\* (Major)

Any substituent at ortho (o) / para (p) / meta of any nature (+M/-M) the electrophile always goes to the positions shown to minimise steric effects