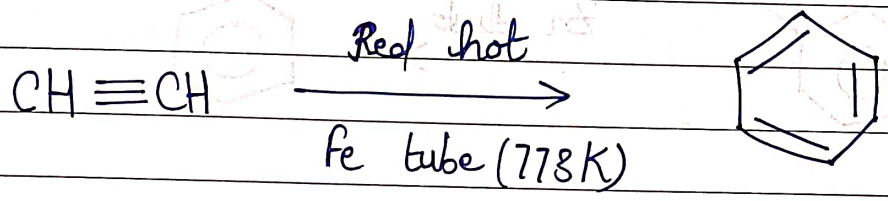
E.A.S

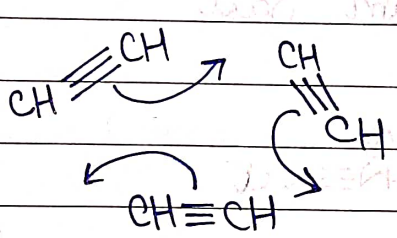
(Electrophilic Aromatic Substitution)

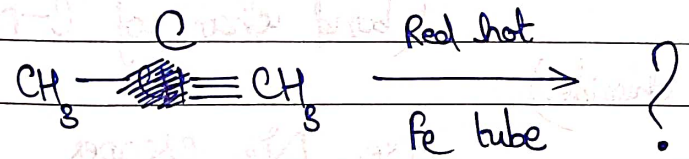
Prepⁿ of Benzene

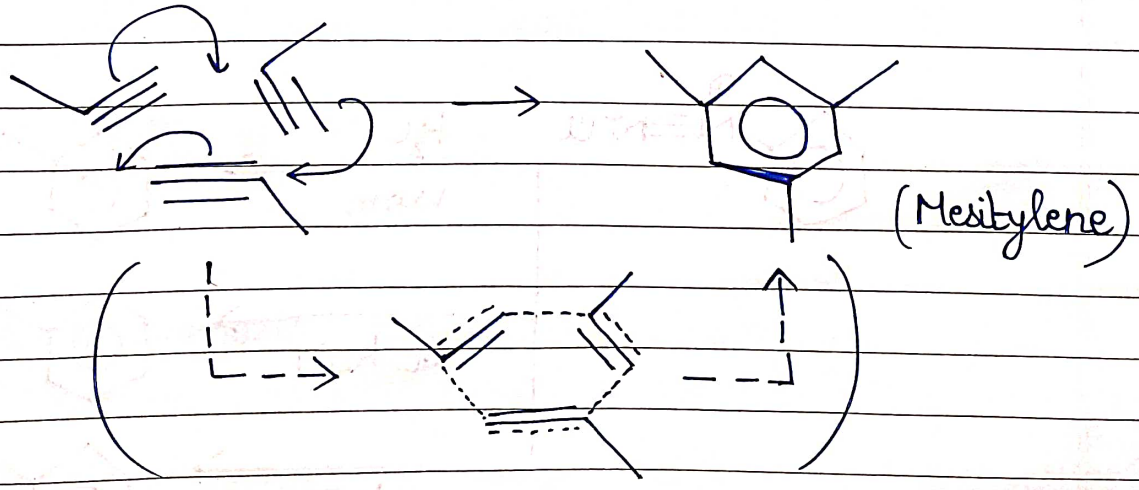
1) Cyclic Polymerisation of Alkyne —



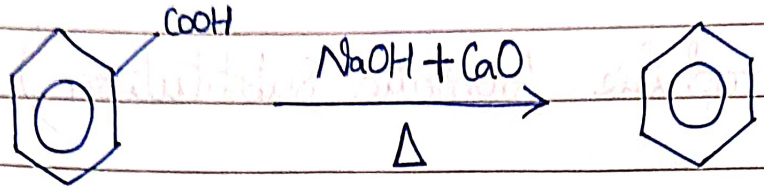
Mechanism :



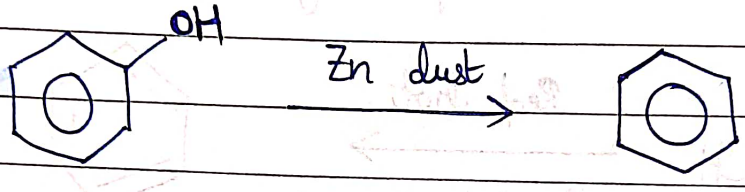
Q) 

A) 

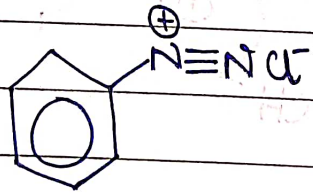
2) Decarboxylation of Aromatic Carboxylic Acids –



3) From Phenol –



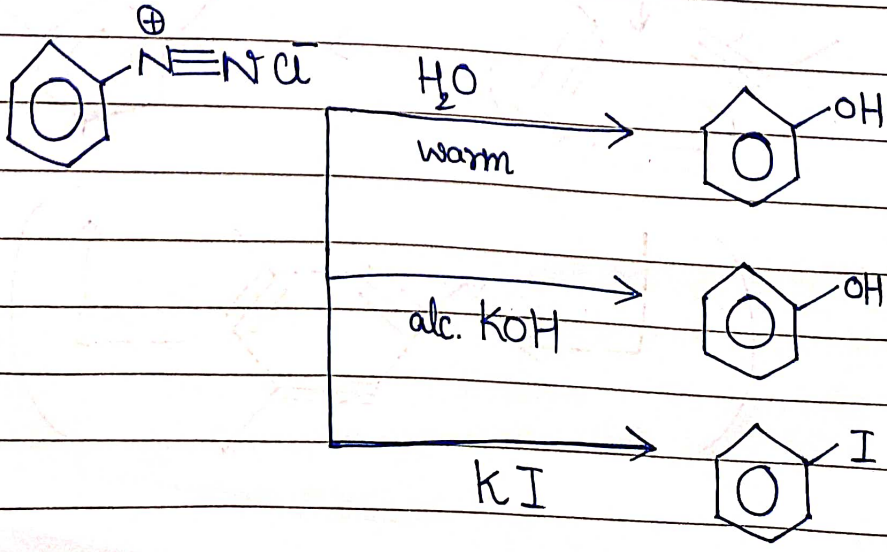
4) From Dizonium Salt –

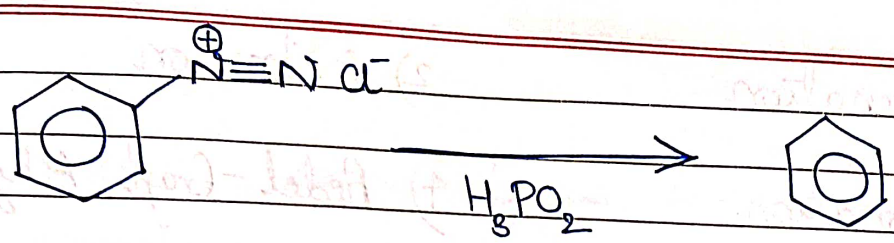


(Benzene dizonium Chloride)

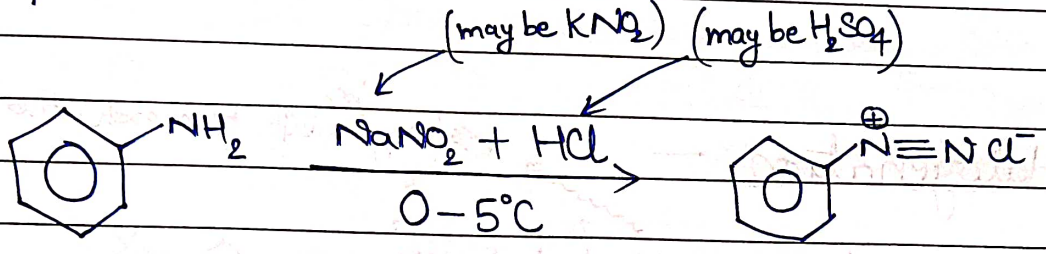
Exists b/w 0°C & 5°C (due to partial double bond char. of C–N)

Else N_2 escapes.



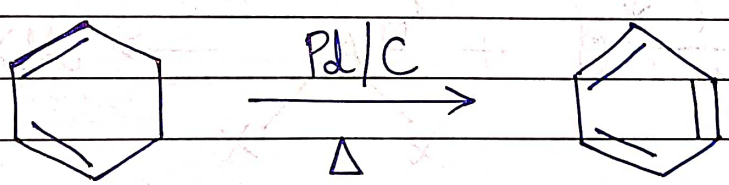


Prepⁿ of Diazonium Salt :



(Aniline)

5) Using Pd/C —

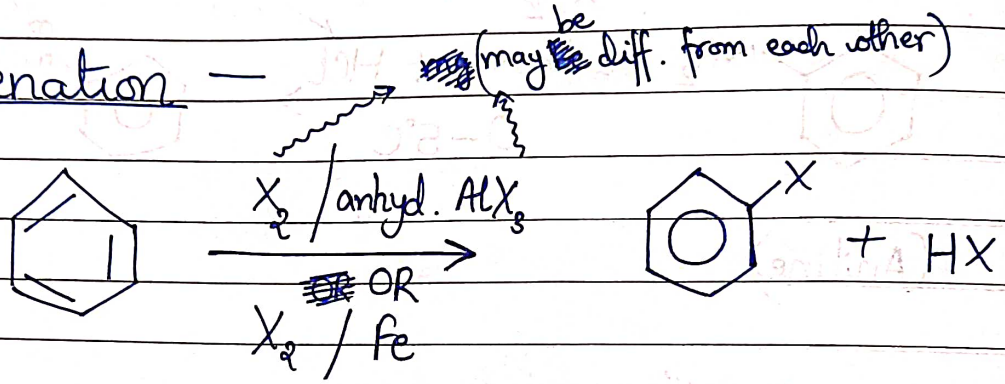


Chem Prop^ts of Benzene

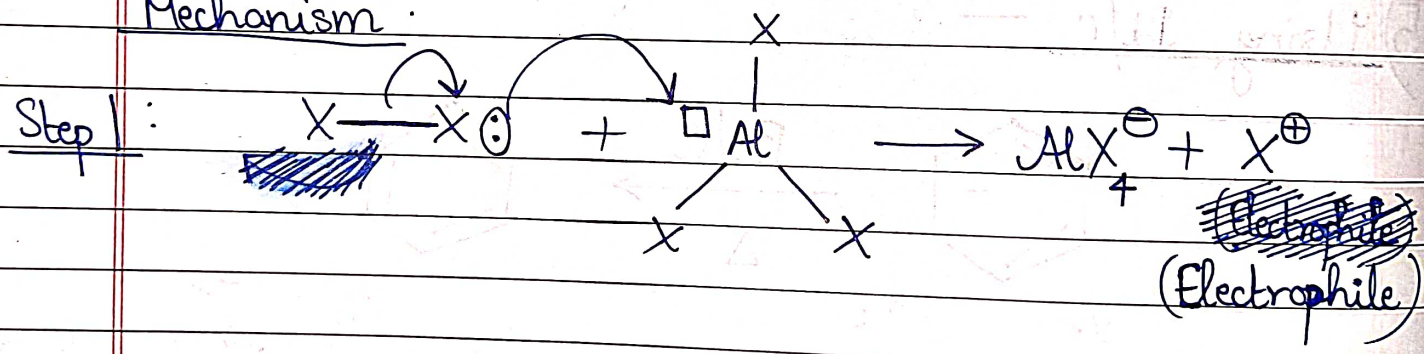
1) Electrophilic Aromatic Substitution —

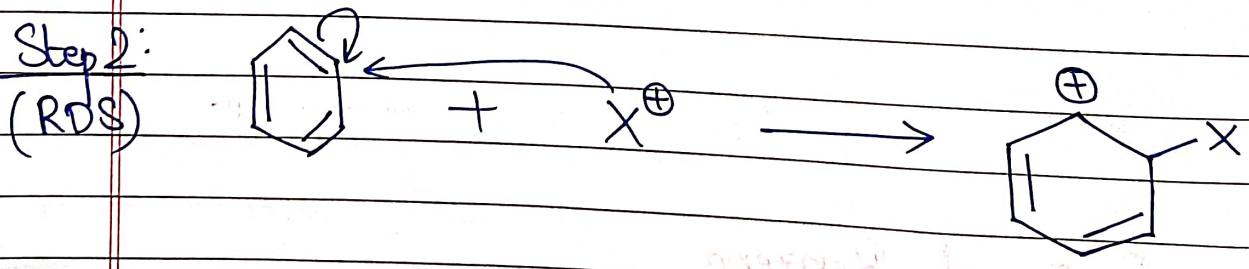
1) Halogenation
2) Nitration
3) Sulphonation
4) Friedel-Craft Alkylation
5) Friedel-Craft Acylation / Acetylation

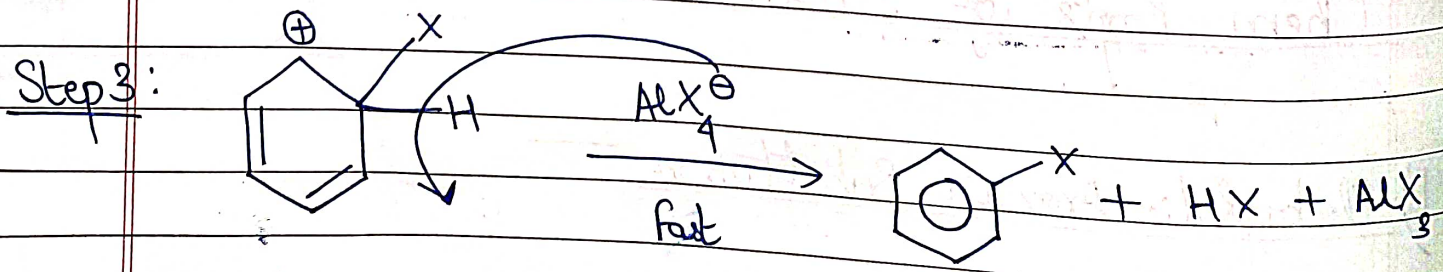
1) Halogenation —



Mechanism:



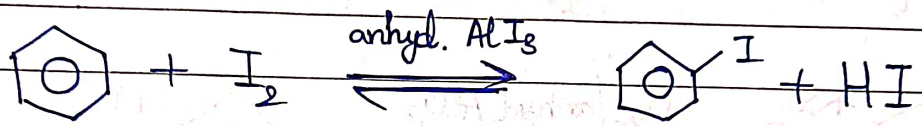




1.1) In step 2, aromaticity is lost.
In step 3, aromaticity is gained.

1.2) F_2 can NOT be used as it is explosive.

1.3) for I_2, all steps are very slow. Hence, all steps necessary to be considered for rate law exp^n
This is because all steps are reversible.



We need strong oxd^n agent (HNO_3, HIO_3, ...)

$$HI + HNO_3 \longrightarrow NO_2 + I_2 + H_2O$$

1.4) Isotopic Effect —

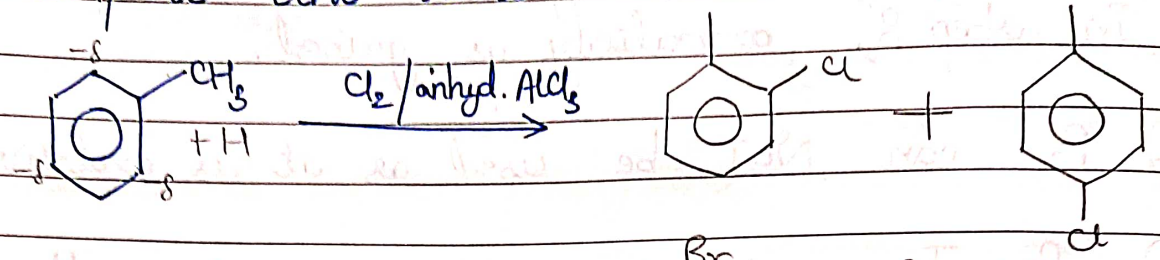
for (Cl_2 / Br_2), $\boxed{r_{C_6H_6} = r_{C_6D_6} = r_{C_6T_6}}$ (As C–H bond break in Step 3 which is NOT Rds)

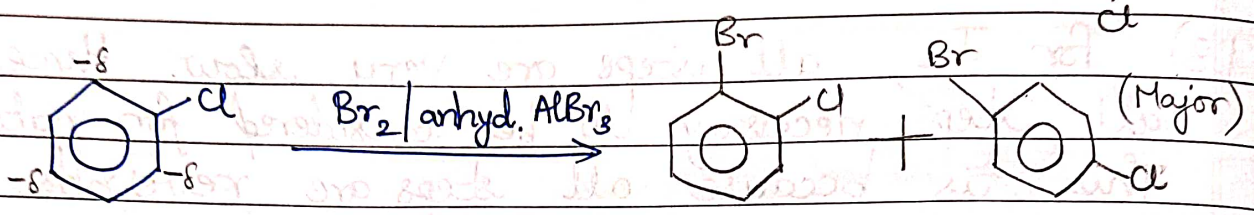
for (I_2), $\boxed{r_{C_6H_6} > r_{C_6D_6} > r_{C_6T_6}}$ (as all steps slow)

☆ Benzene & its derivatives do NOT give E⊕ add^n rx^{n}s as in those rx^{n}s aromaticity is lost.

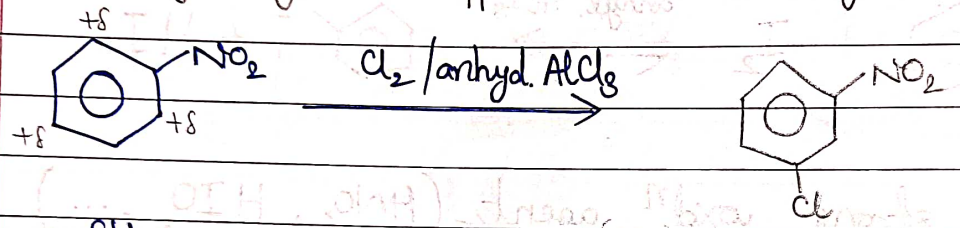
(Major Product unless H bond in ortho

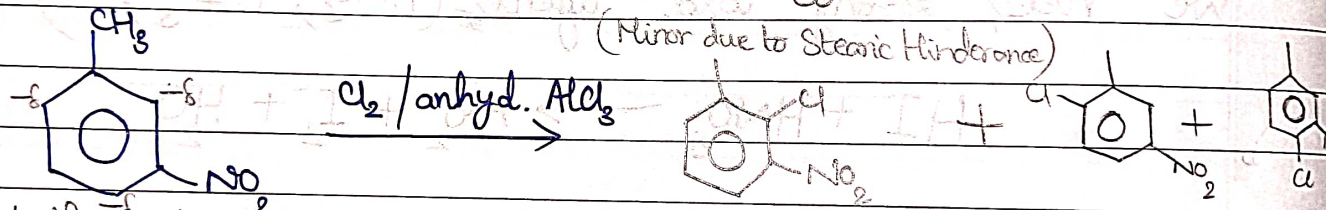
★ Q) Complete the rxns —

1) 

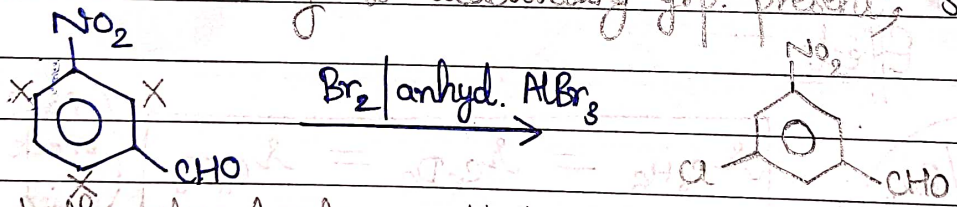
2) 

(Even though −I very strong, rxn happens thru res. & halogens have +M effect)

3) 

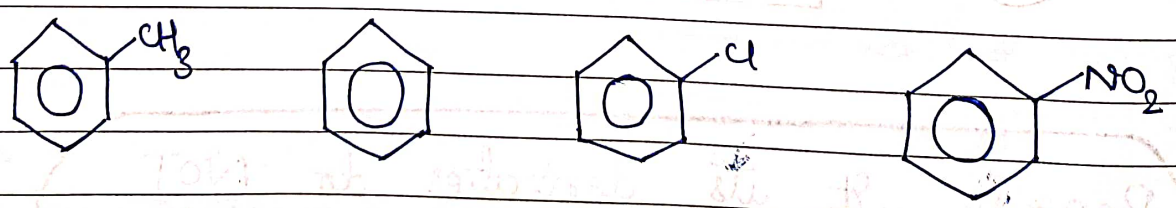
4) 

(When both activating & deactivating grp. present, see only activating grp.)

5) 

(When both deactivating, block pat. due stronger deactivating grp.)

Q) Compare rate of E.A.S.



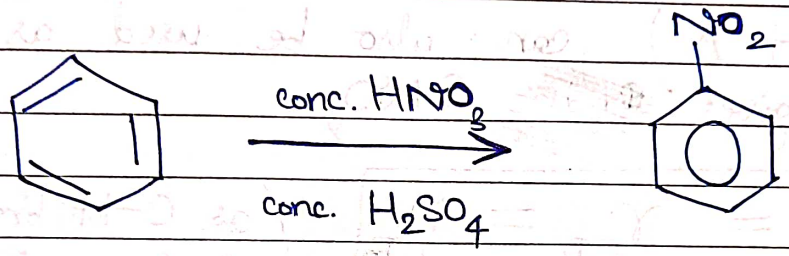
A) a > b > c > d

+H −I > +M −M & −I

☆ for checking reactivity, see net effect.
for checking product, see res. effects.

☆ (Reactivity in EAS) ∝ (e⁻ density in ring)

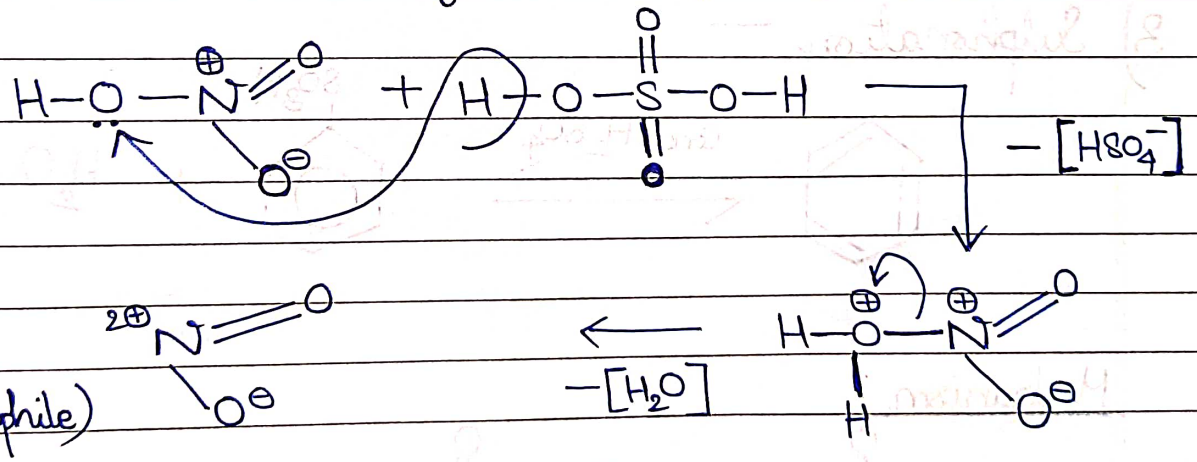
2) Nitration —



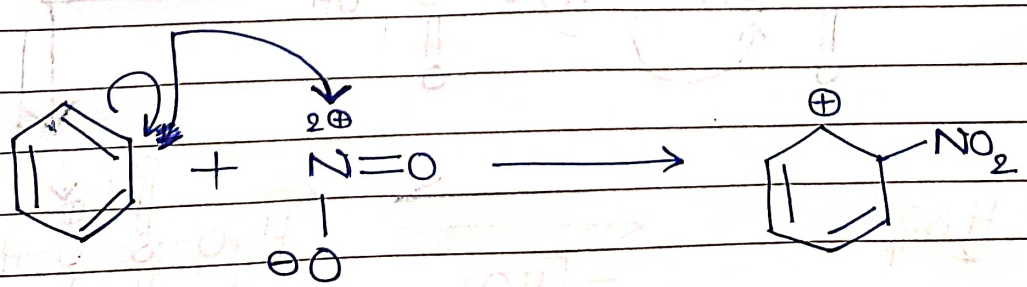
Mechanism: Acidic: $H_2SO_4 > HNO_3$
Oxd^n agent: $HNO_3 > H_2SO_4$

~~Step 1:~~

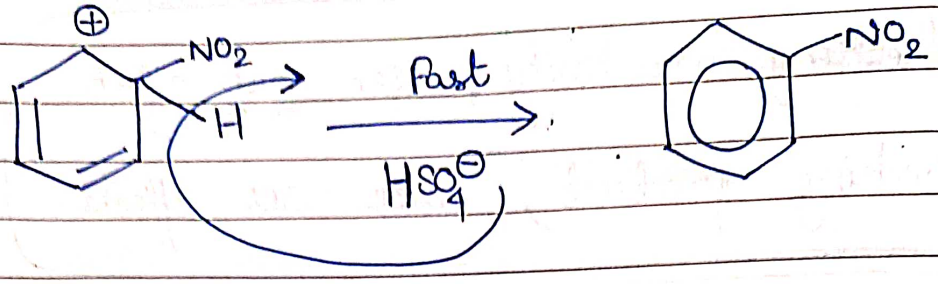
Step 1:



Step 2: (RDS)



Step 3 :

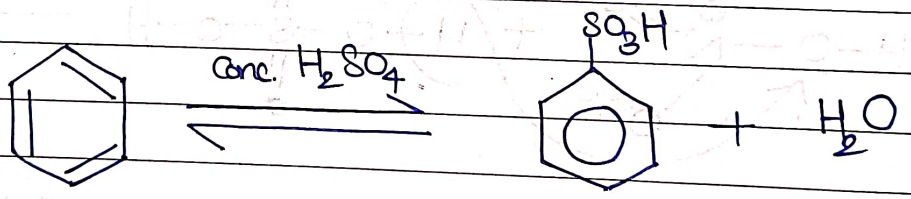


2.1) HNO_3 acts as a Base.

2.2) $(N_2O_5 + \Delta)$ can also be used as it gives $\oplus NO_2$

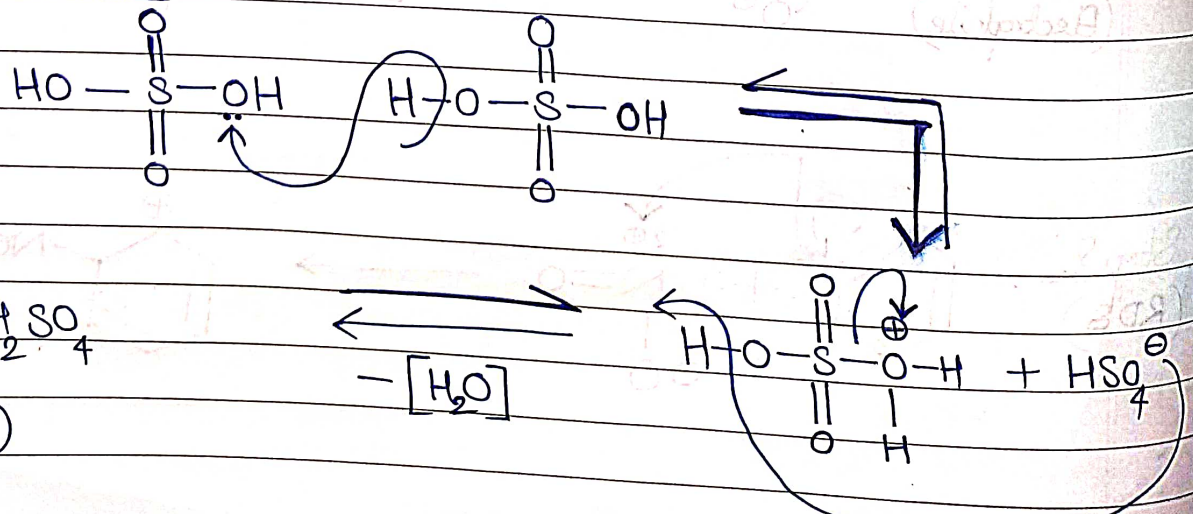
2.3) $\boxed{r_{C_6H_6} = r_{C_6D_6} = r_{C_6T_6}}$ (as C–H break in Step 3 which is NOT Rds.)

3) Sulphonation —

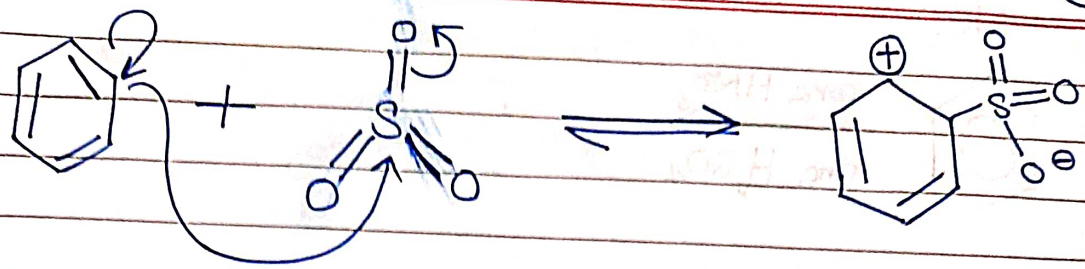


Mechanism :

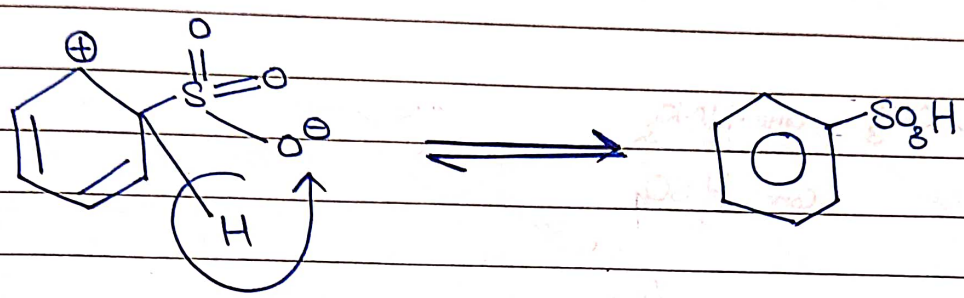
Step 1 :



Step 2 :



Step 3 :

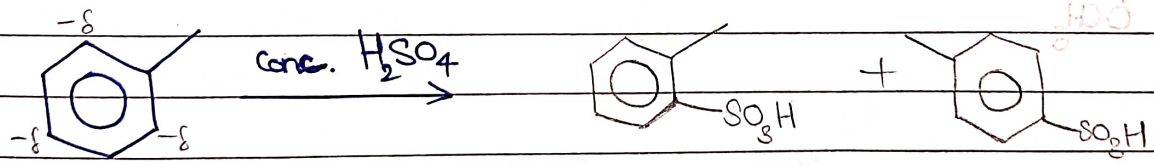


3.1) Electrophile is neutral (SO_3)

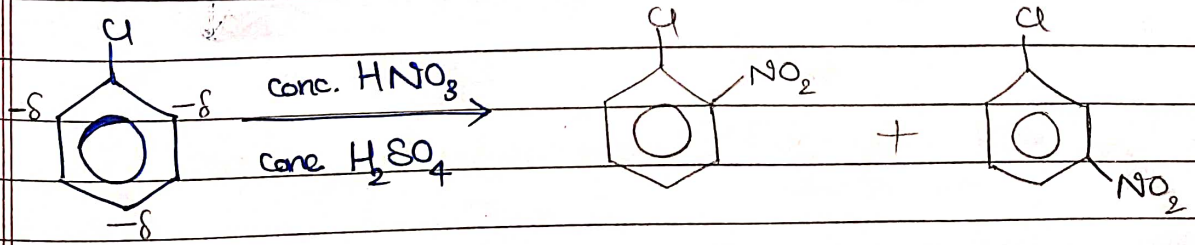
3.2) $\boxed{r_{C_6H_6} > r_{C_6D_6} > r_{C_6T_6}}$ (as all steps are reversible & contribute in rate law exp^n)

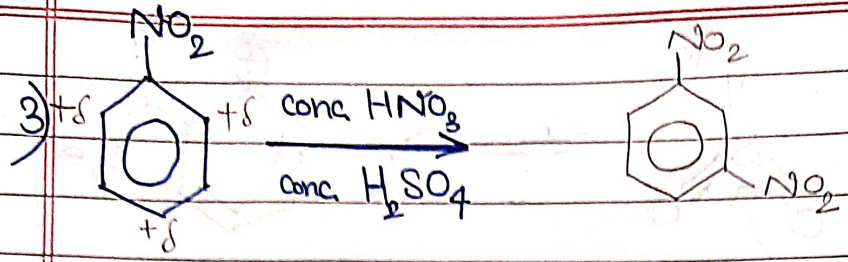
Q) Complete the rx^{n}s —

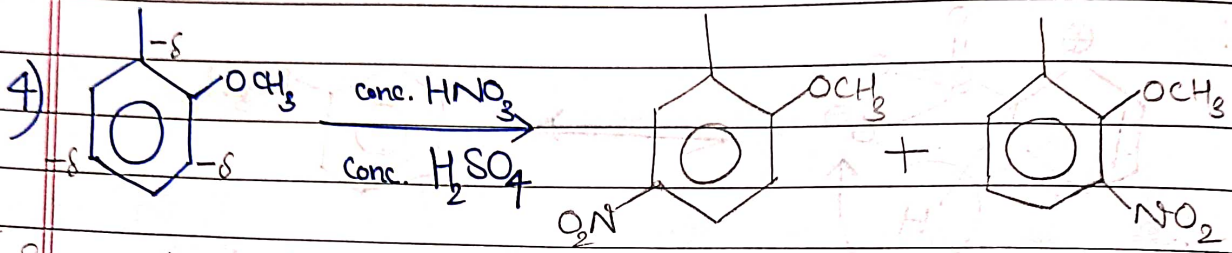
1)



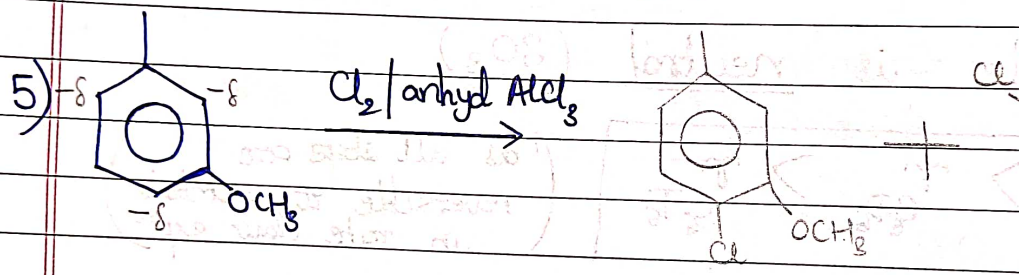
2)

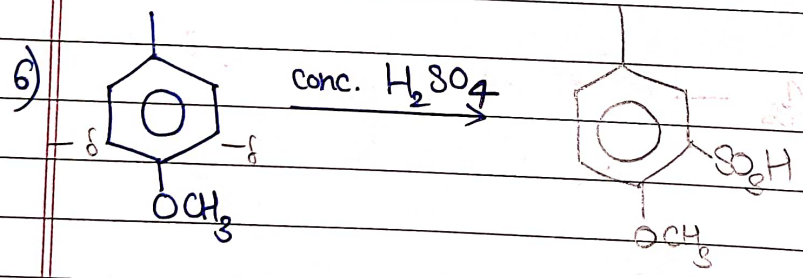


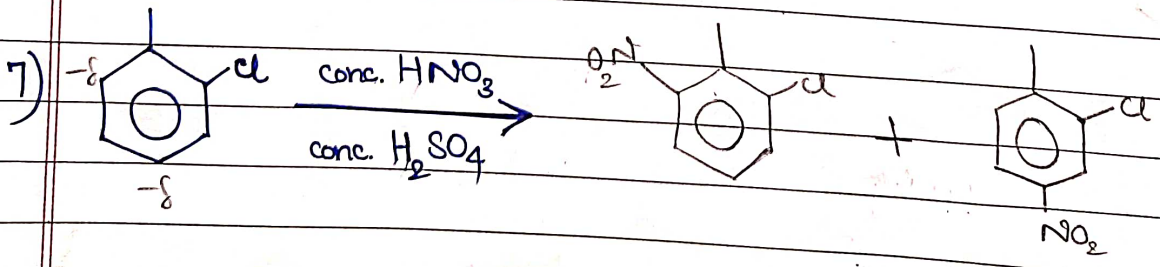
3) 

4) 

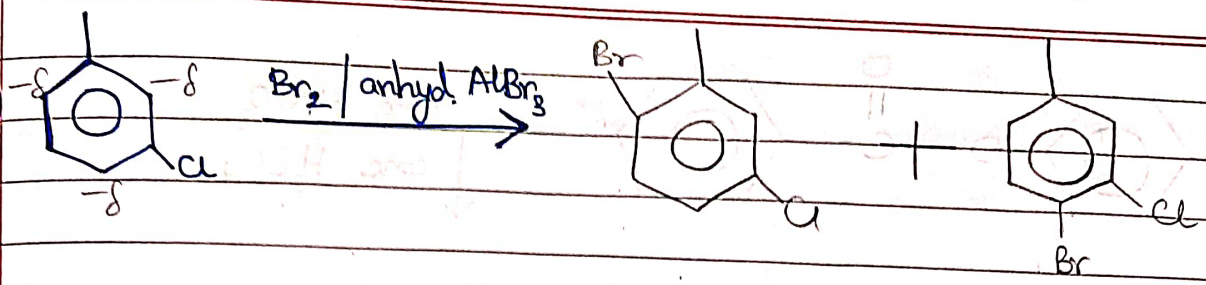
(See wrt stranger activating grp., when 2 activating grps pres

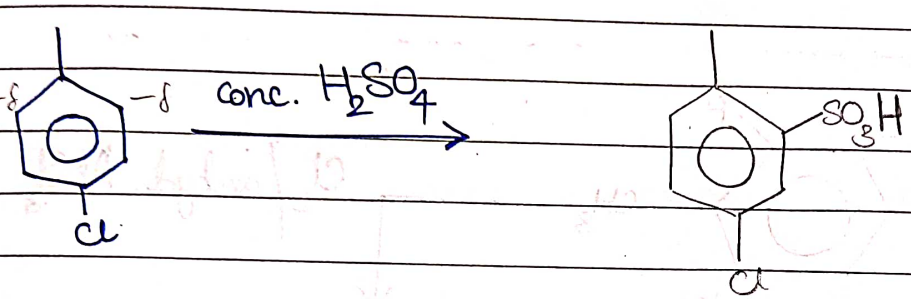
5) 

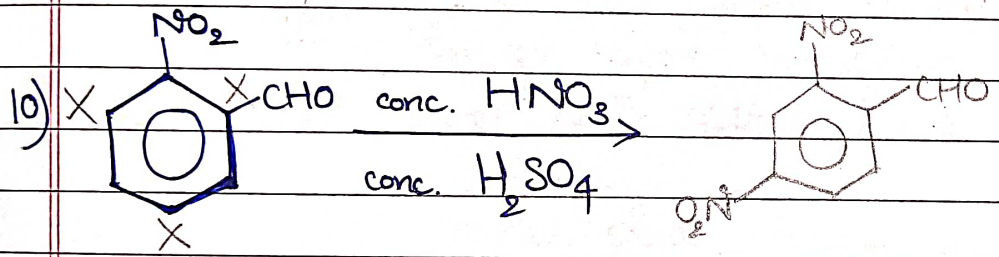
6) 

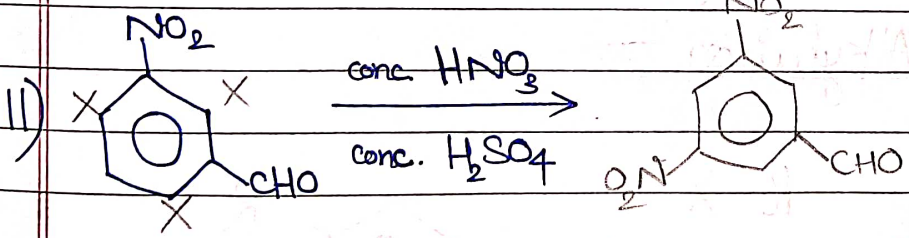
7) 

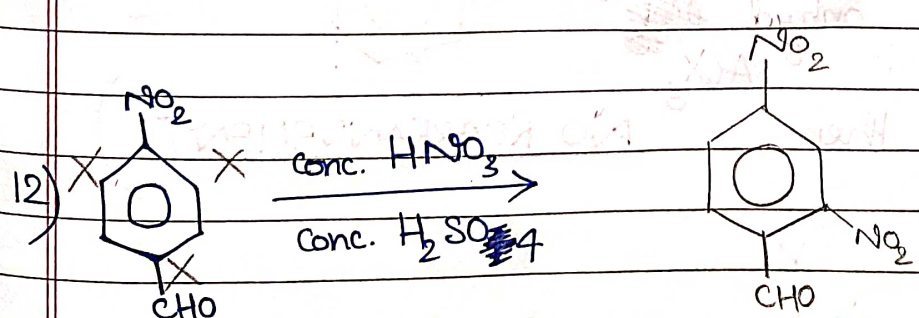
(See wrt CH_3 as it is more activating than Cl)

8) 
Br2 / anhyd. AlBr3
Br
Cl
Cl
Br

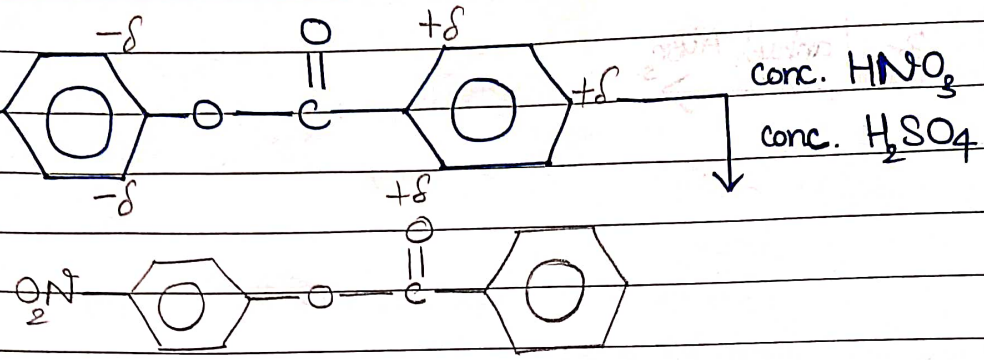
9) 
conc. H2SO4
SO3H
Cl

10) 
NO2
CHO
conc. HNO3
conc. H2SO4
NO2
CHO
O2N

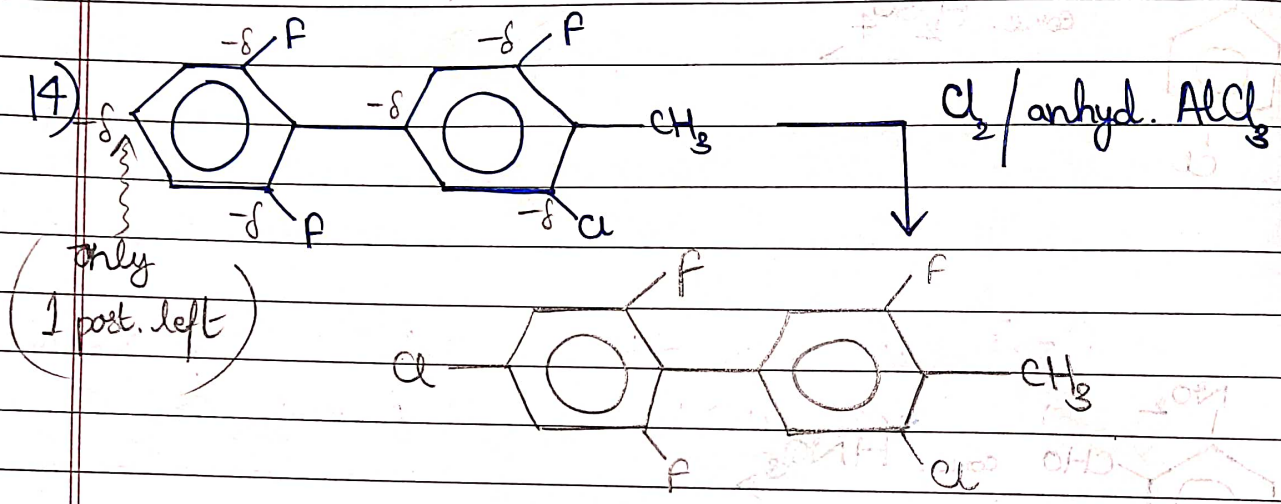
11) 
NO2
CHO
conc. HNO3
conc. H2SO4
NO2
O2N
CHO

12) 
NO2
CHO
conc. HNO3
conc. H2SO4
NO2
NO2
CHO

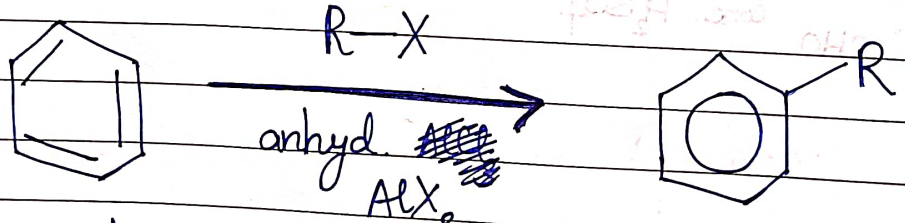
13)



14)



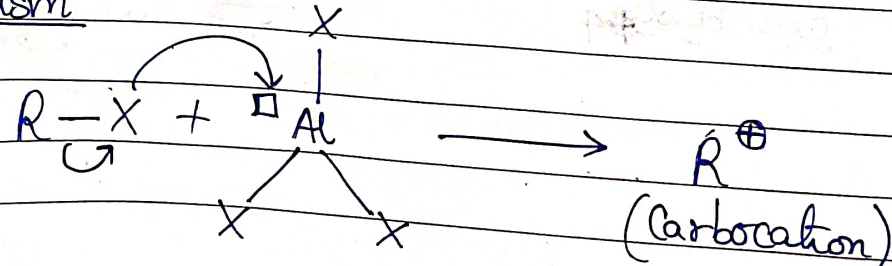
4) Friedel Craft Alkylation —



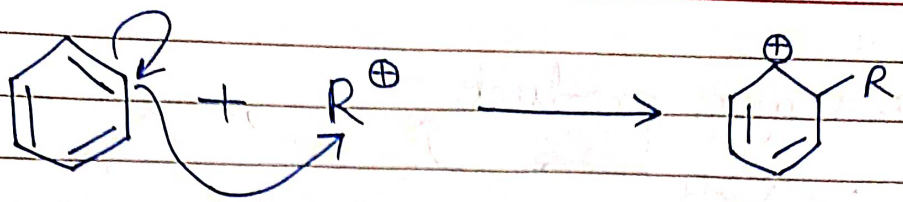
(if $FeCl_3$ is used, then NO REARRANGEMENT)

Mechanism :

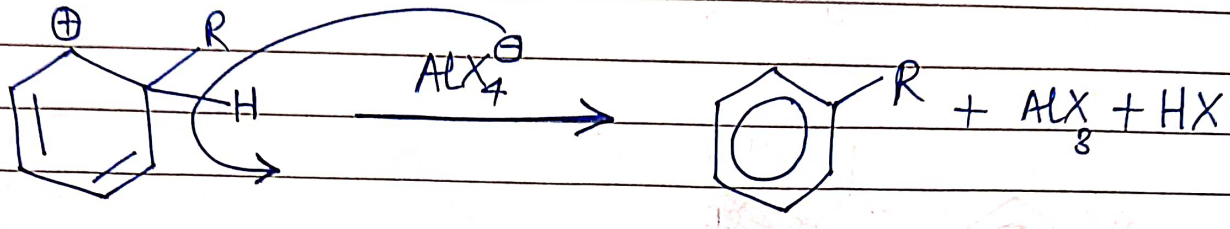
Step I :



Step 2: [RDS]



Step 3:



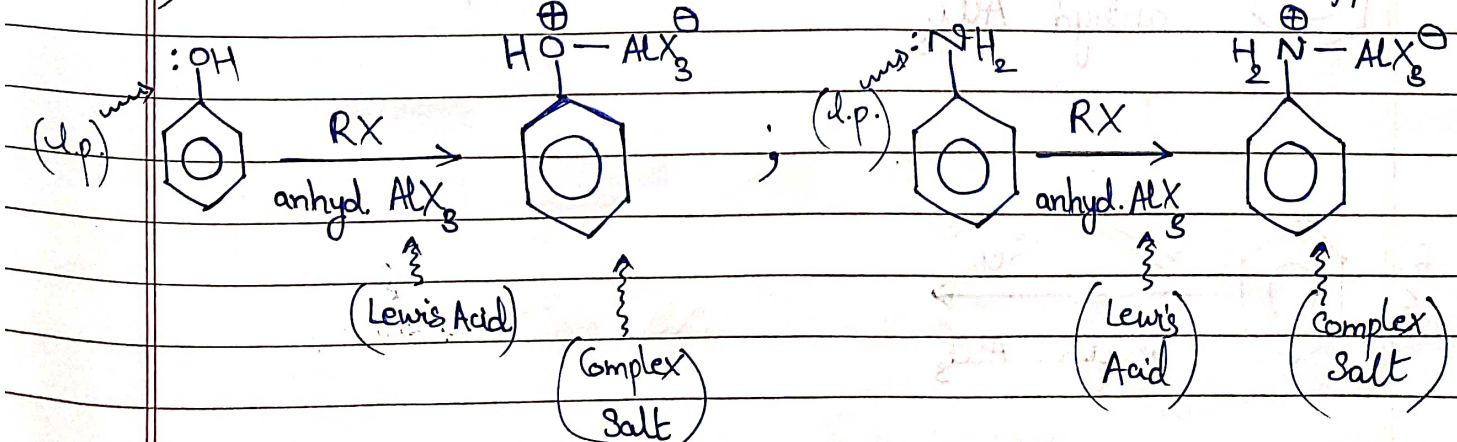
4.1) Carbocation is formed ⇒ Rearrangement is possible.

4.2) If R–X is in ~~excess~~ excess, alkyl derivative of  being more reactive (as R is activating grp.) the rx^n does NOT stop here.

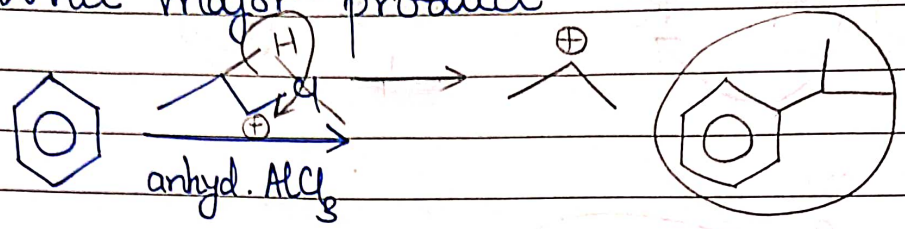
further EAS takes place. Hence, multiple R grps. may join.

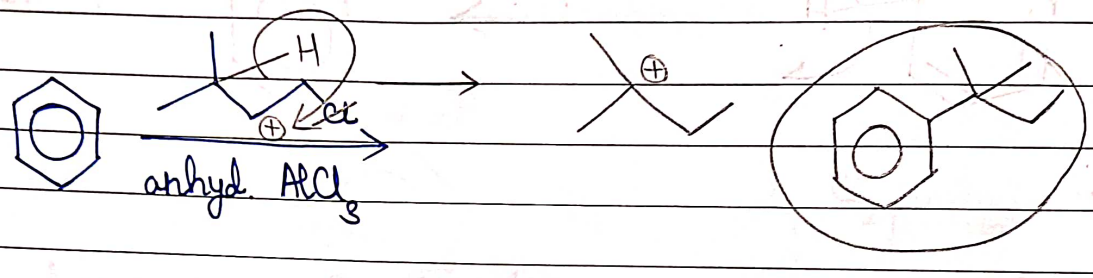
4.3) If deactivating grp ($-NO_2$, $-CN$, $-COOH$, $-CHO$, ...) is attached to ring, then this rx^n NOT possible.

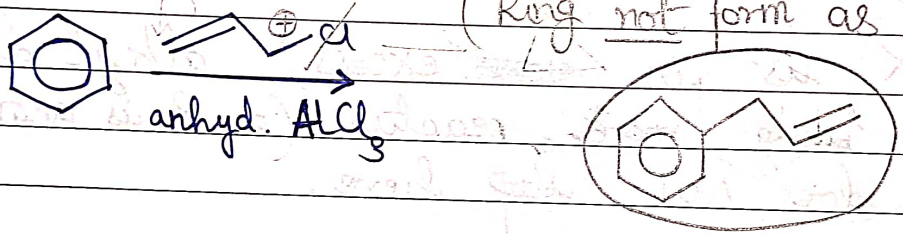
4.4) With Phenol & Aniline, this rx^n NOT happens.



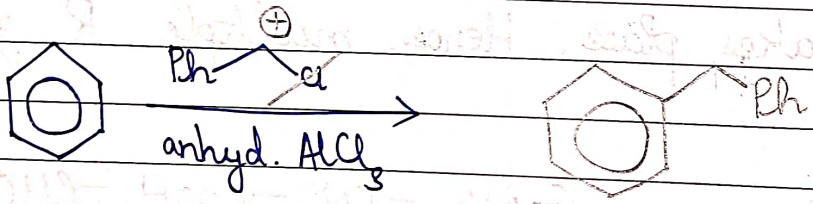
Q) Write major product —

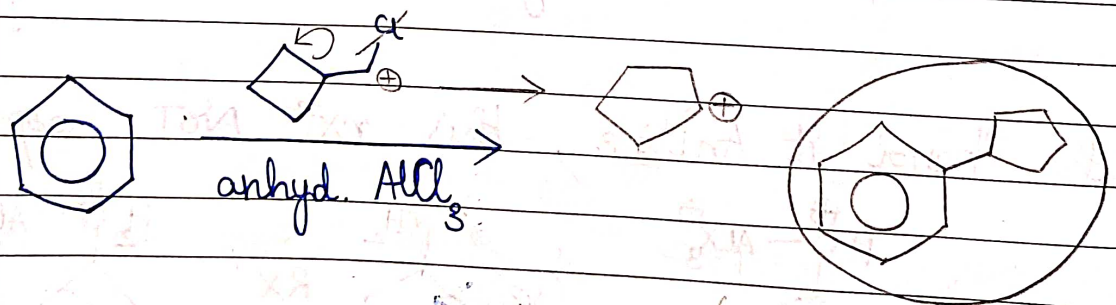
1) 

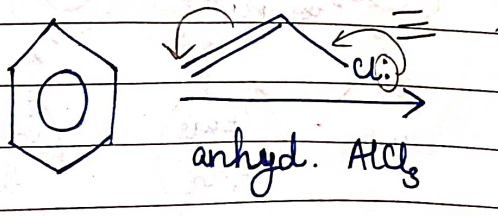
2) 

3) 

(Ring not form as ring strain)

4) 

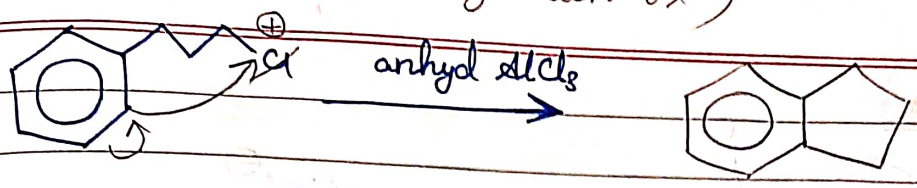
5) 

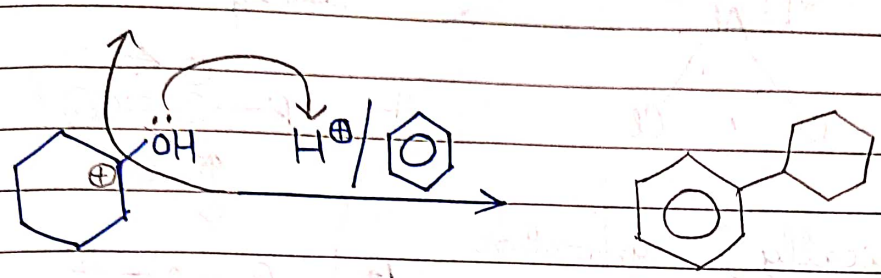
6) 

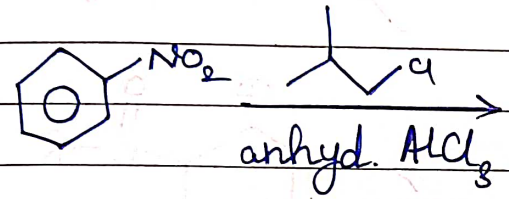
(partial double bond char)

No rxn

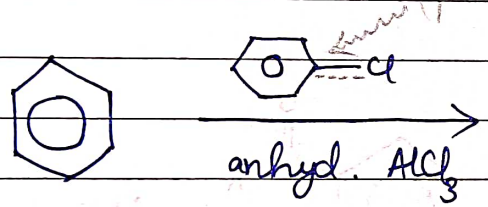
(Intramol. F.C. alkylation rxn)

8) 

9) 

10) 

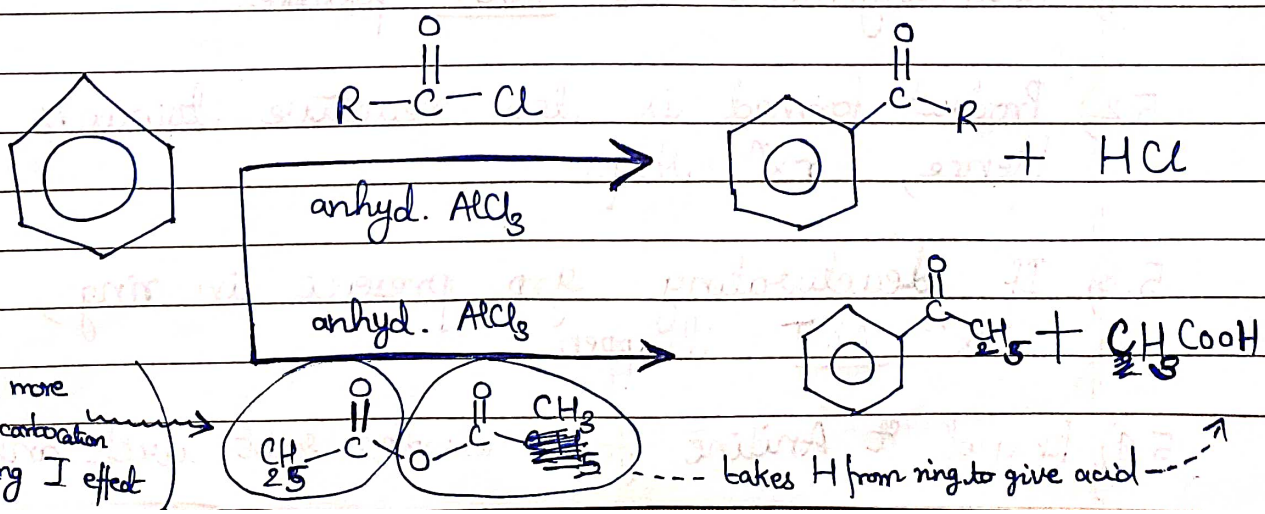
No rxn

7) 

No rxn

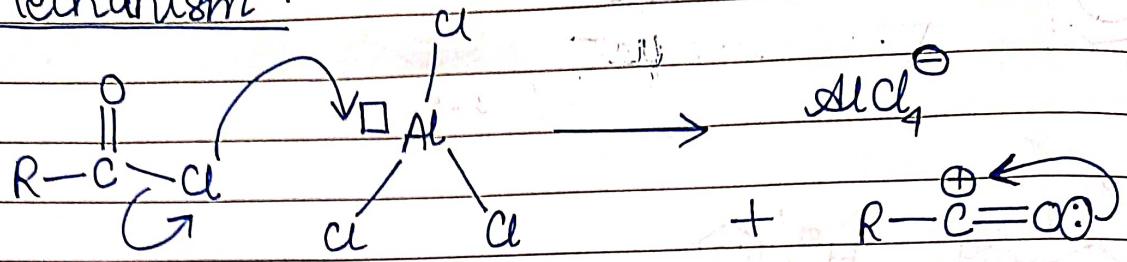
☆ If both F.C. alkylation & acetylation possible, then acetylation happens first.

5) Fiedel Craft Acetylation —



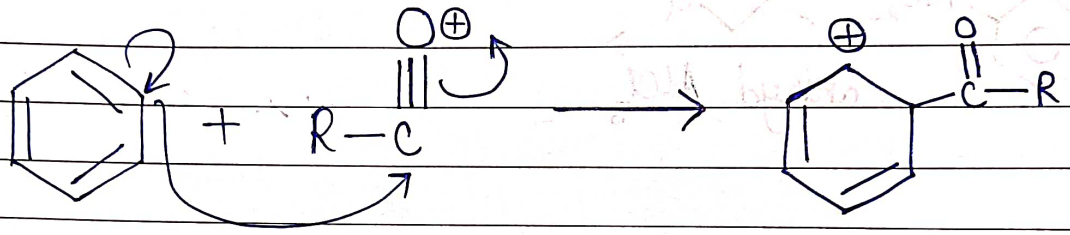
Mechanism:

Step 1:

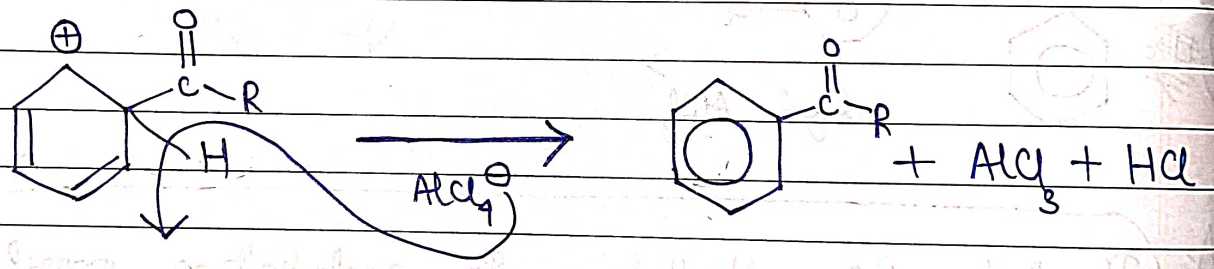


(Since, technically, carbocation NOT formed ⇒ No Rearrangement)

Step 2: (RDS)



Step 3:



(In case of 2nd rxn in prev. page bottom, the H alongside $-\overset{O}{\overset{\|}{C}}-R$ is taken to form acid by $\ominus O-\overset{O}{\overset{\|}{C}}-CH_3$)

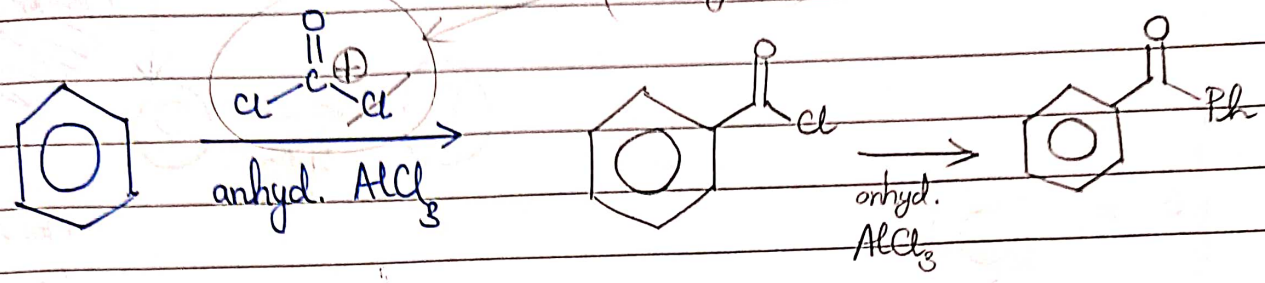
5.1) Rearrangement is NOT possible.

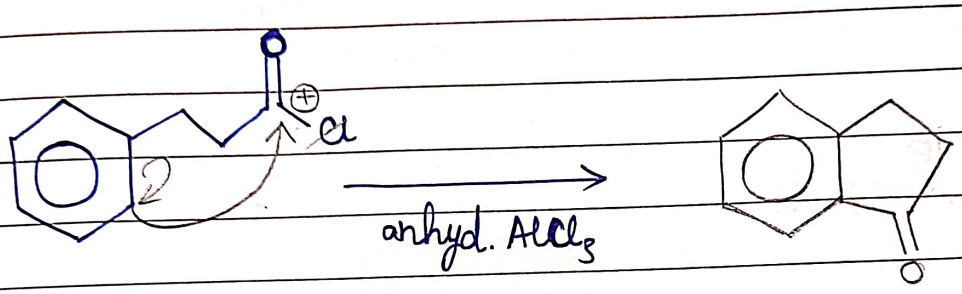
5.2) Product formed is less reactive towards EAS. Hence, rxn stops.

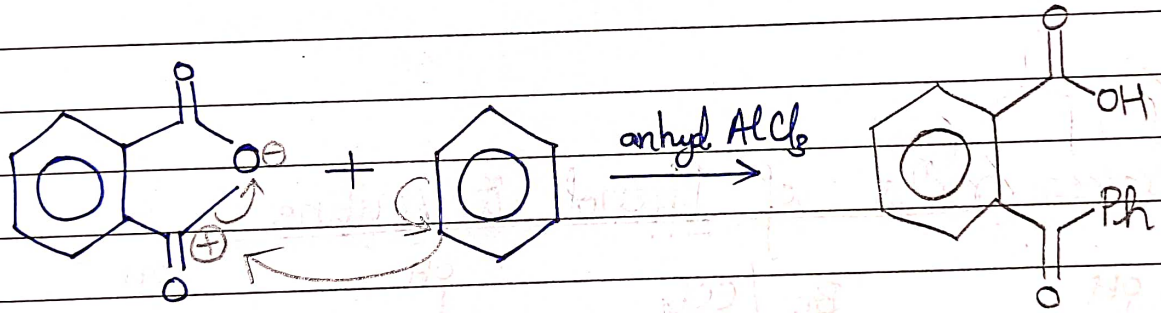
5.3) If deactivating grp. present in ring, then this rxn NOT happen.

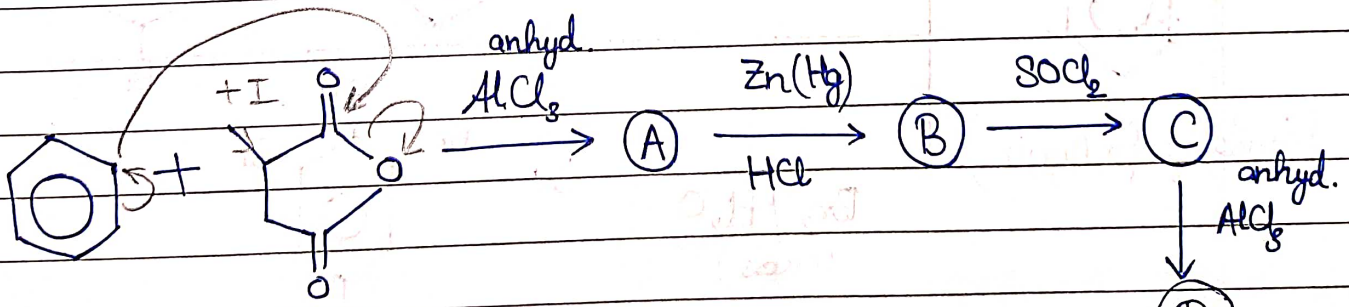
5.4) Phenol & Aniline form complex salt with anhyd. AlX_3

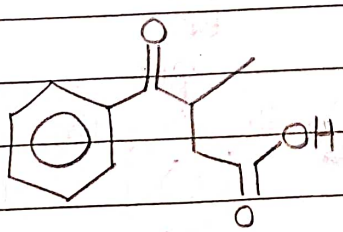
Q) Write major product —

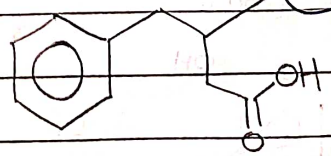
1) 

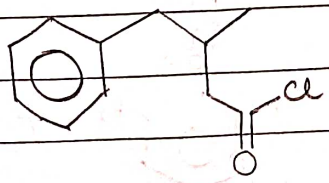
2) 

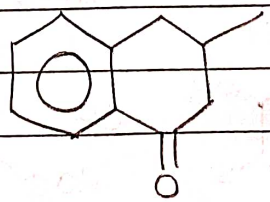
3) 

4) 

A = 

B = 

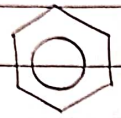
C = 

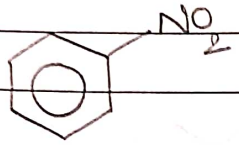
D = 

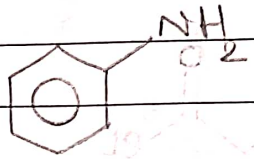
5) $C_2H_2 \xrightarrow[\text{red hot}]{Fe} (A) \xrightarrow[H_2SO_4]{\text{conc. } HNO_3} (B) \xrightarrow{Sn/HCl} (C)$

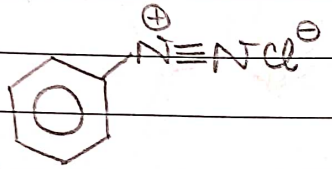
(C) $\xrightarrow[0-5^\circ C]{NaNO_2 + HCl}$ (D) $\xrightarrow{H_3PO_2}$ (E)

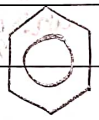
$NaNO_2 + HCl$ (0–5°C)

A = 

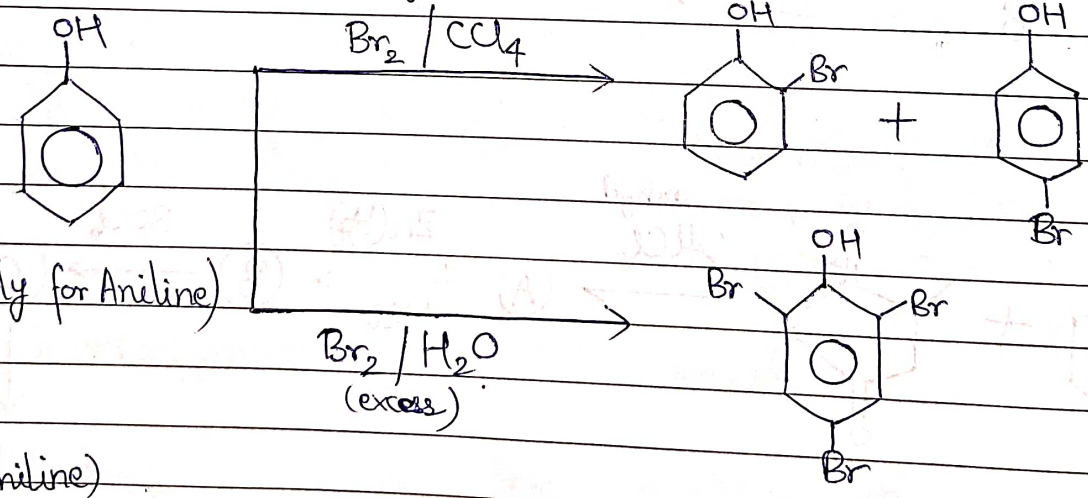
B = 

C = 

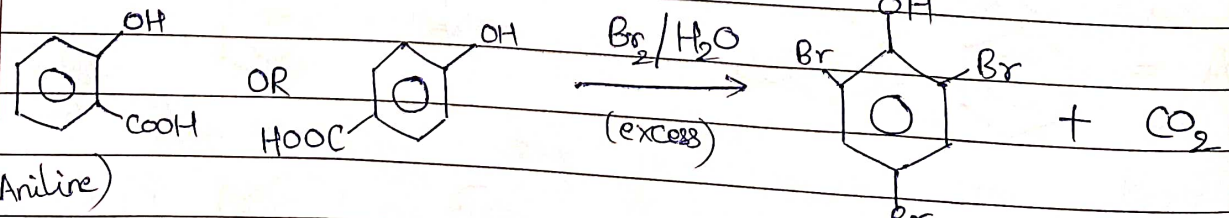
D = 

E = 

Some rxn's of Phenol & Aniline

1) 

(Similarly for Aniline)

2) 

(Similarly for Aniline)

3)