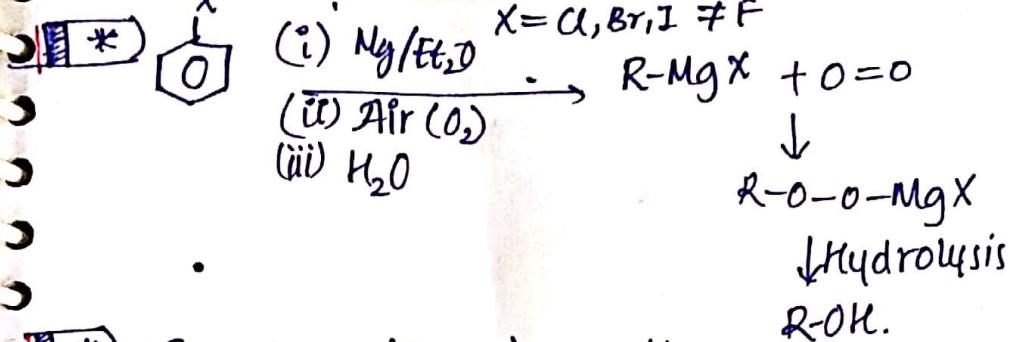


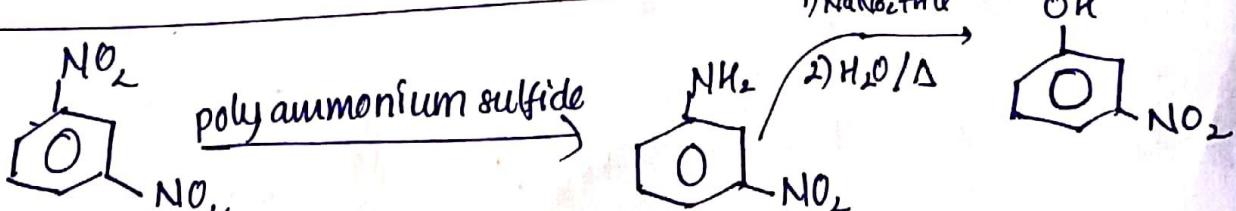
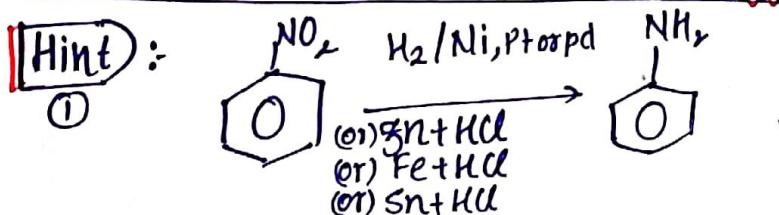
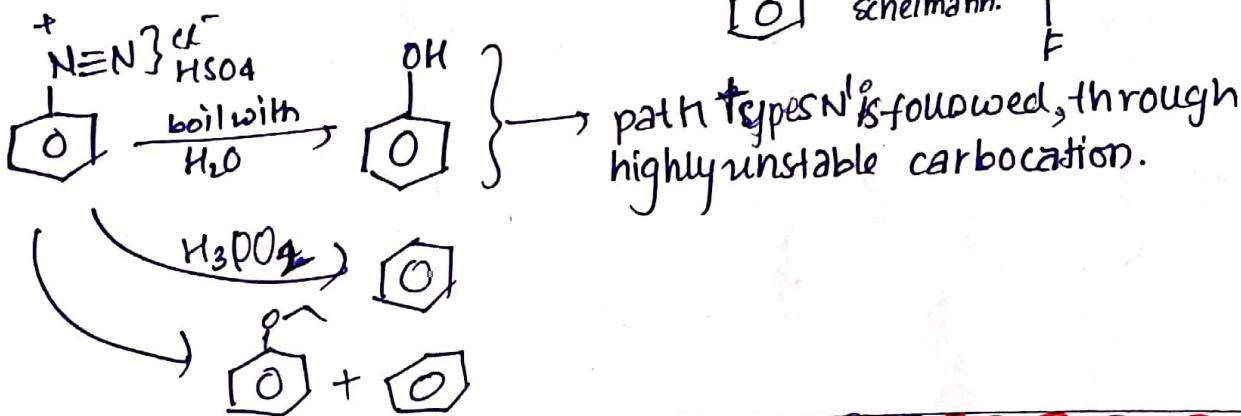
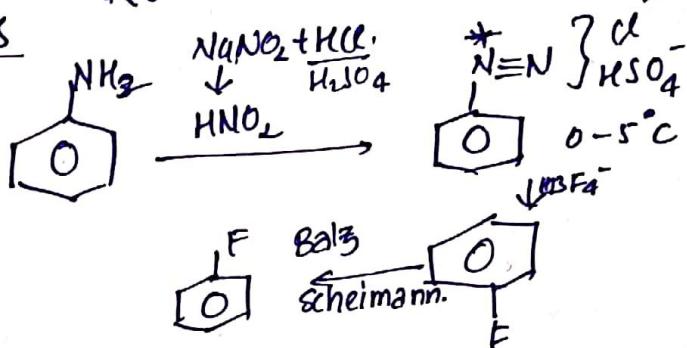
* PHENOLS *

Preparation of phenol (carbolic acid)

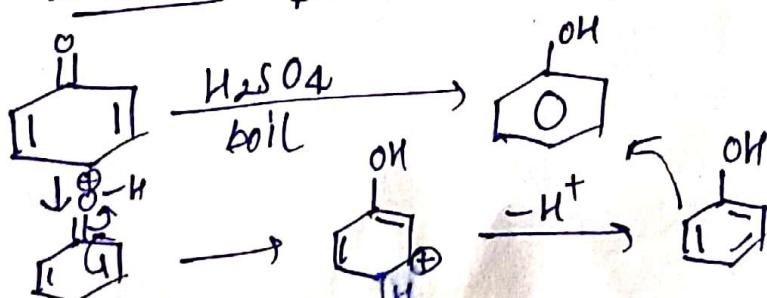


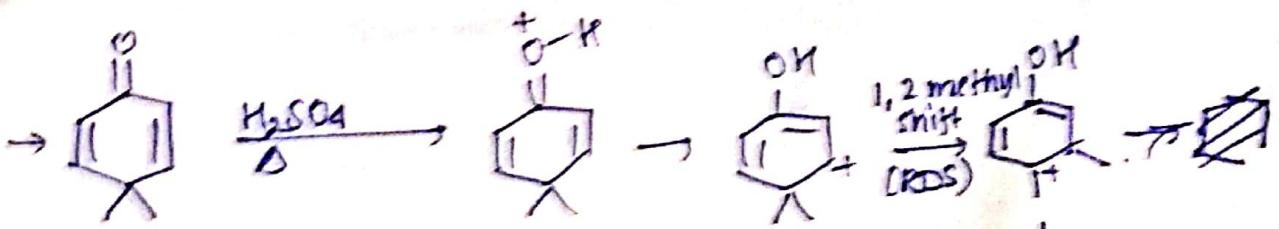
By using diazonium salts

↑ Diazotisation
 only aromatic primary amines.

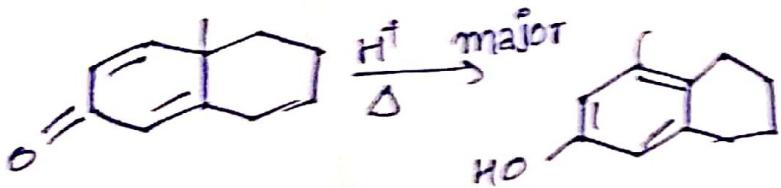
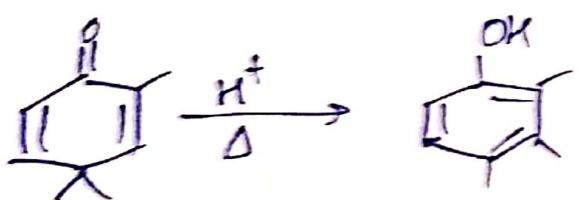
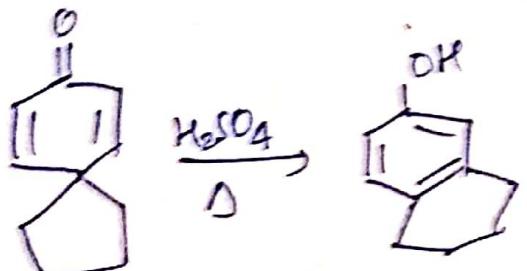
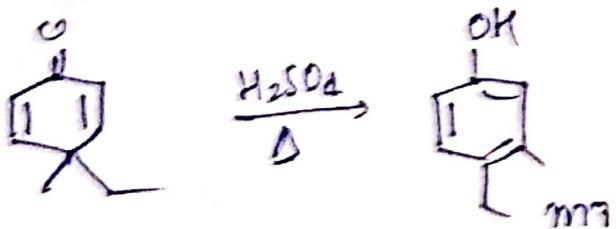


Dieneone-phenol rearrangement

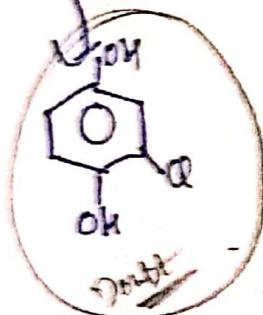
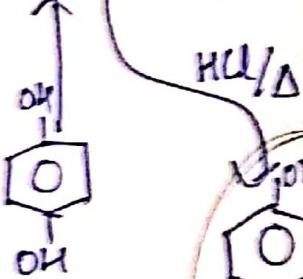




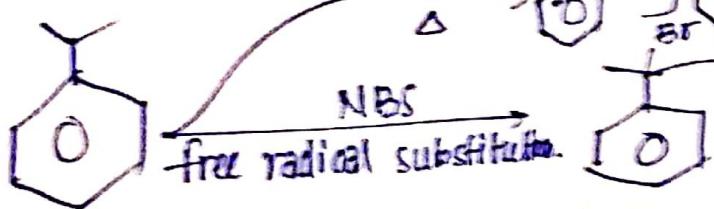
To attain aromaticity the very slow RDS step occurs.



* Industrial fact (Imp. for Adv.)



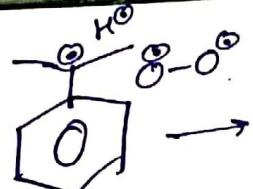
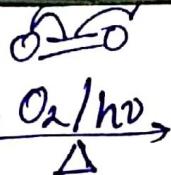
* Cumine usage in prep. of phenol



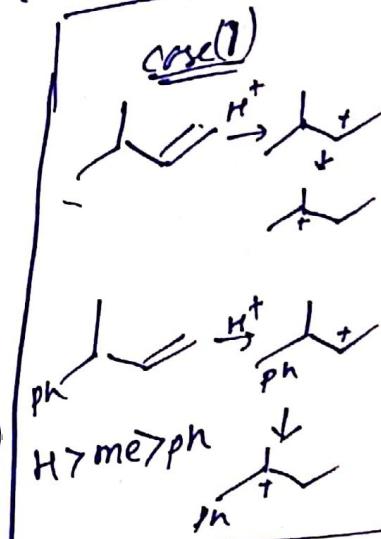
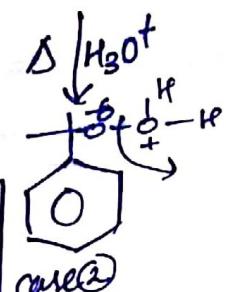
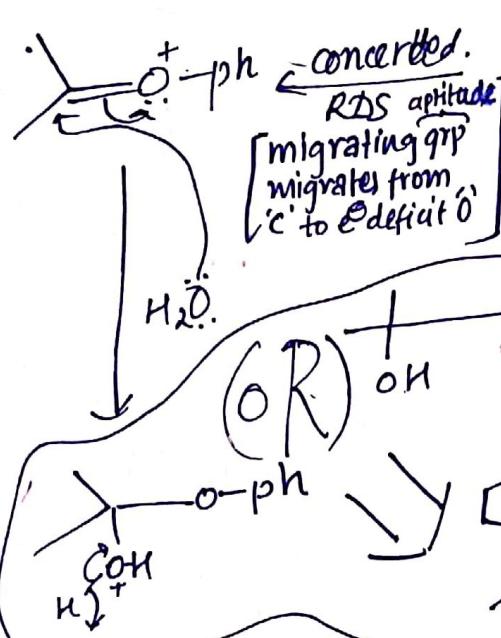
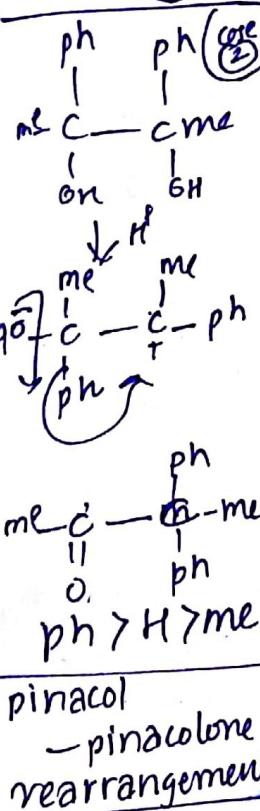
At least one benzylic H is required to convert to benzoic acid. + 2CO₂



2016 Adm
PI

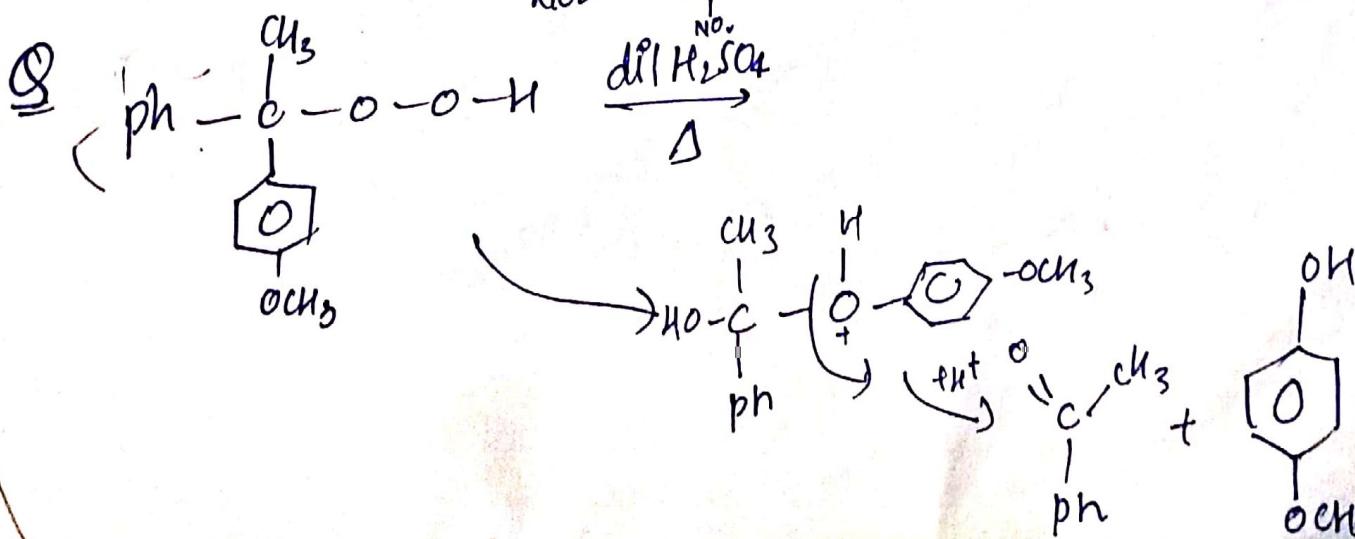
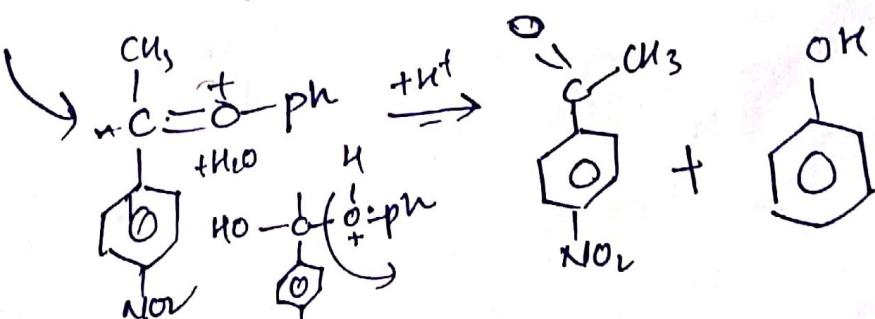
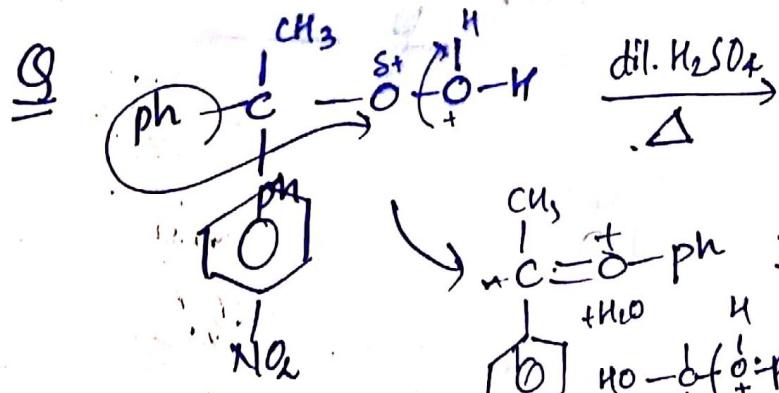


cumene
Hydroperoxide.

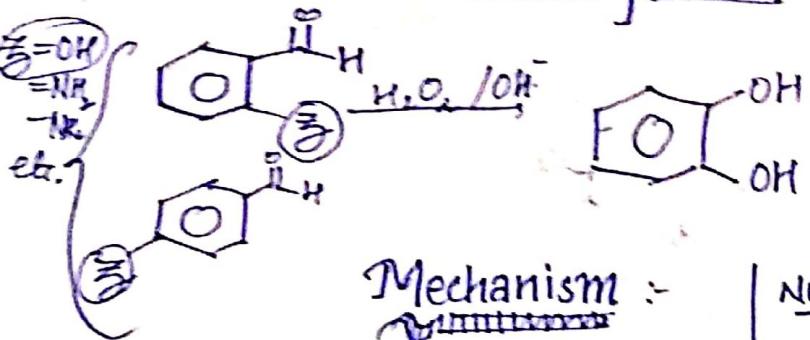


Wagman
and Merwin
rearrange-
ments

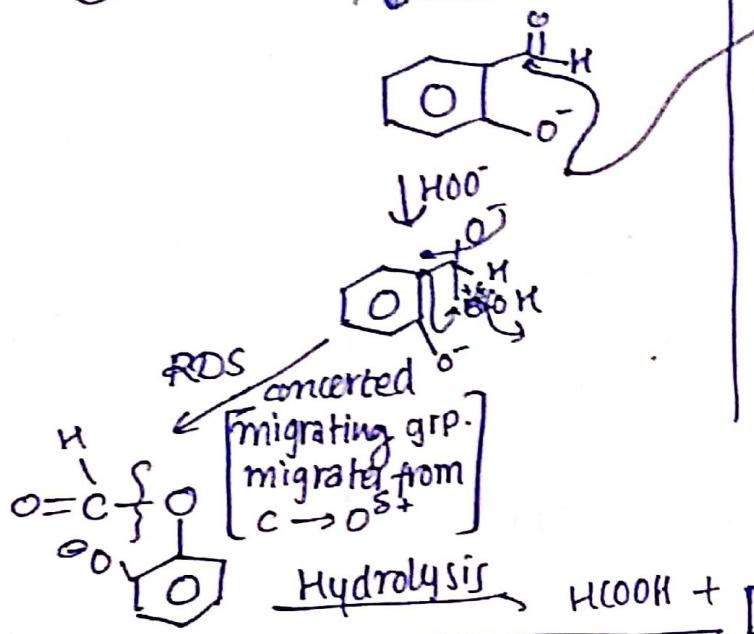
cumene Hydro peroxide rearrangement.



* Dakin's Rearrangements.

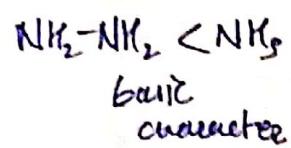
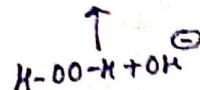
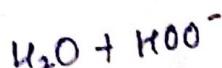


Mechanism :-

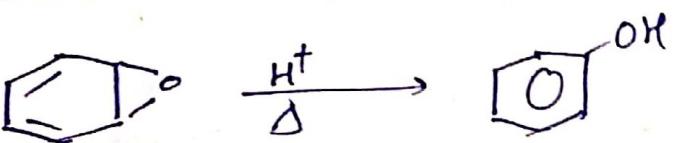


Nucleophilicity

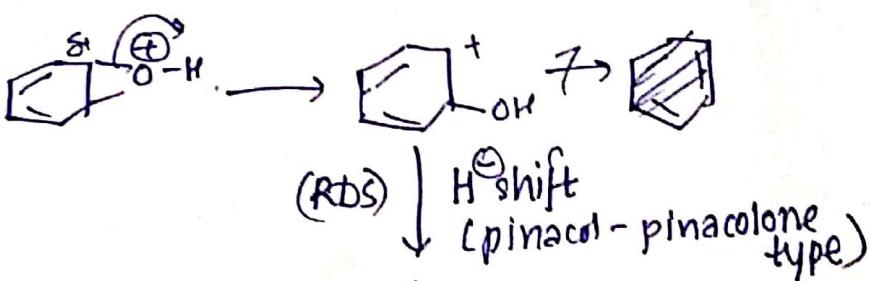
$\text{HO}^- > \text{KO}^- > \text{H}_2\text{O}$
explanation related to coordination chemistry

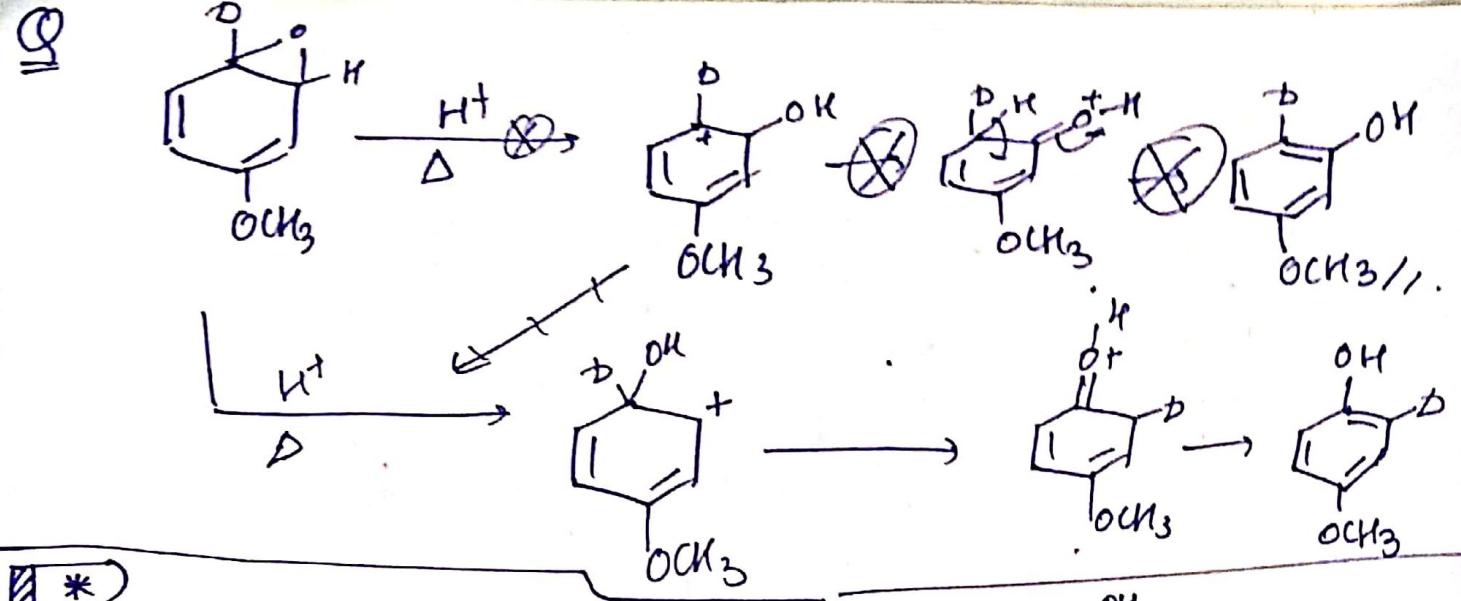


* Arenoxide rearrangement

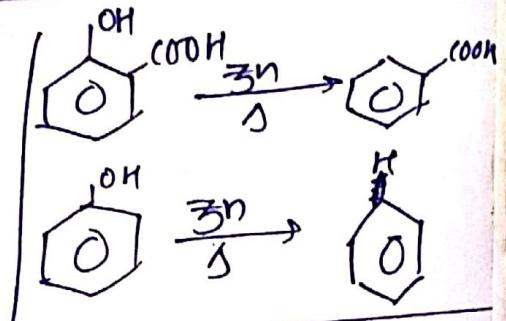
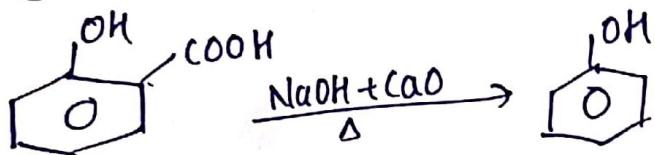


Mechanism :-





~~By using Sn/O~~ By using soda lime



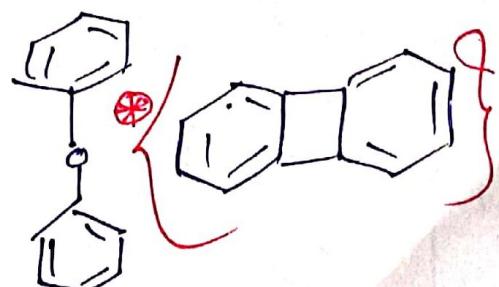
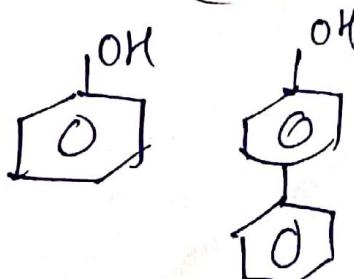
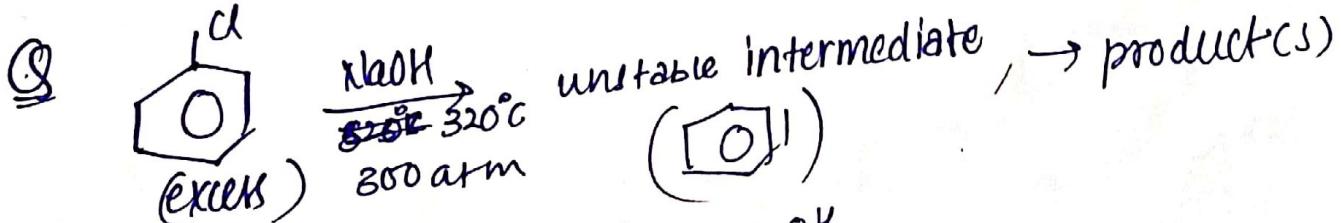
* from halobenzene

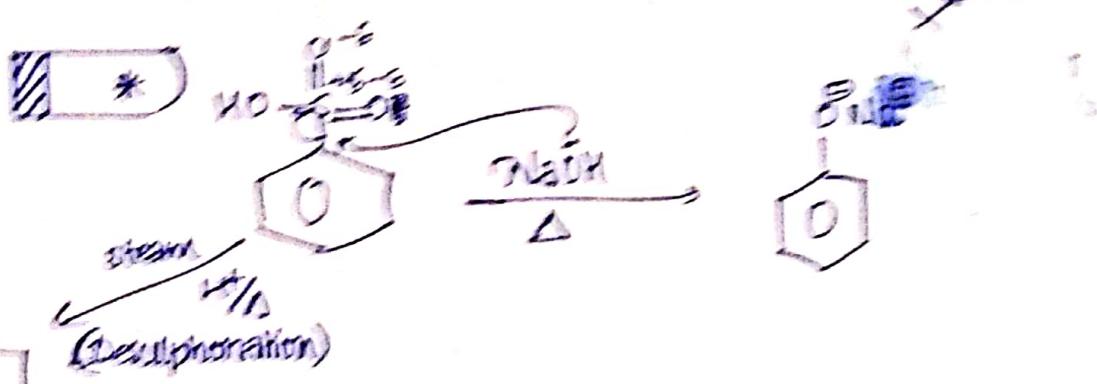
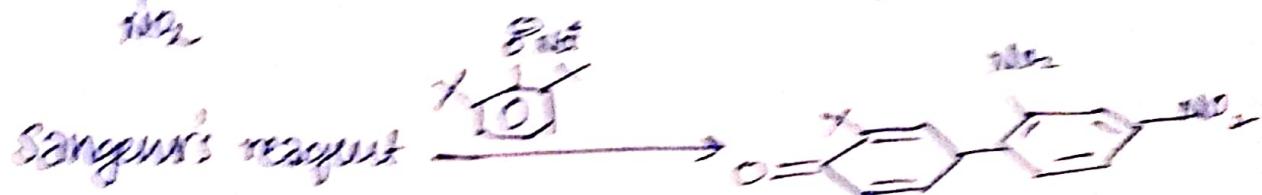
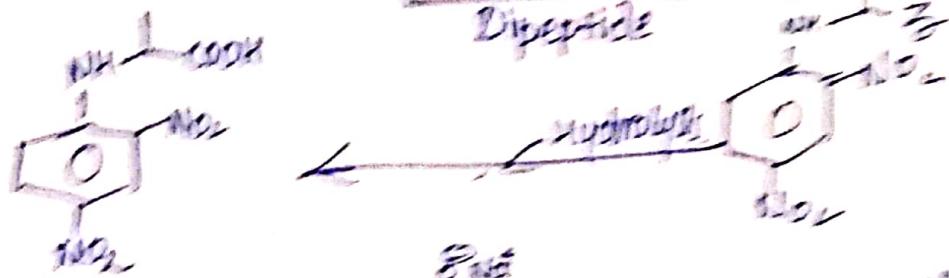
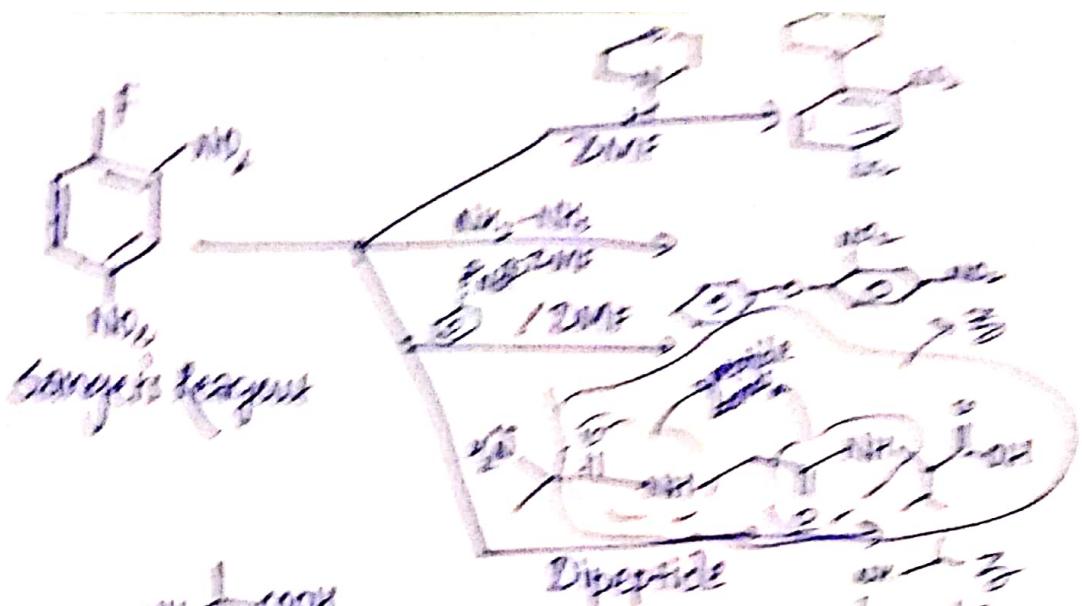
(A) from elimination-addition
(or) Zelinsky's process (or) Benzyne mech.
(or) cine substitution

} High temperature
and strong base

(B) Addition
- Elimination.

(or) Meisenheimer complex } strongly
EWG ars.





Properties of phenols

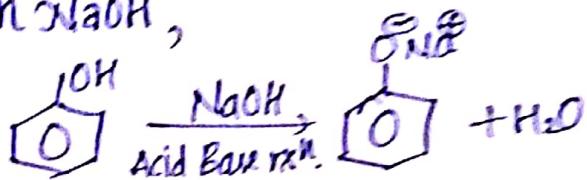
→ pure phenol is solid (white)

→ Melting point 40°C .

→ insoluble in H_2O . (due to hydrophobic ring)

→ density = 1.07 g/cc. [similarly, aniline is also insoluble].

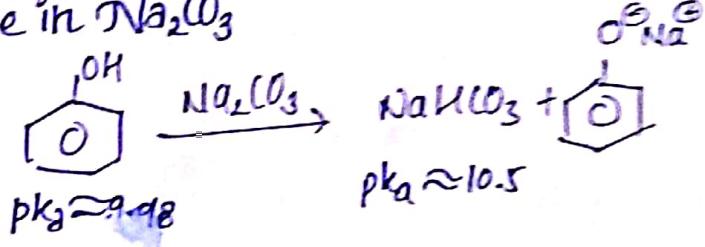
→ Soluble in NaOH ,



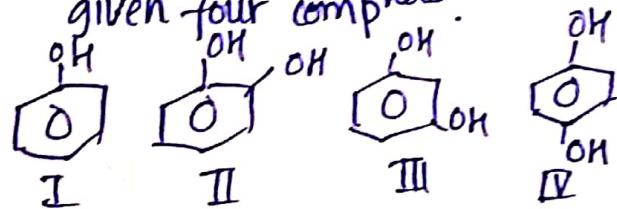
→ Insoluble in NaHCO_3

$$\text{H}_2\text{CO}_3 \text{ p}_{\text{Ka}} \approx 6.5$$

→ Soluble in Na_2CO_3



Q correct in b/w following about given four compounds.



μ :- is zero in none of them.

~~K_a :- $\text{I} < \text{II} < \text{III} < \text{IV}$~~

~~$\text{B.P.} :- \text{IV} > \text{III} > \text{II} > \text{I}$~~

Inter
molecular
 H -bonding

Intra
molecular
 H -bonding



(1) Alkylation rxn / Acylation (or) Acetylation

~~(i)~~ Nucleophilicity ($\text{N} \text{U}^-$): $\text{R}-\text{NH}_2 > \text{R}-\text{O}^- > \text{R}-\text{OH}$ (w.r.t. reagents)

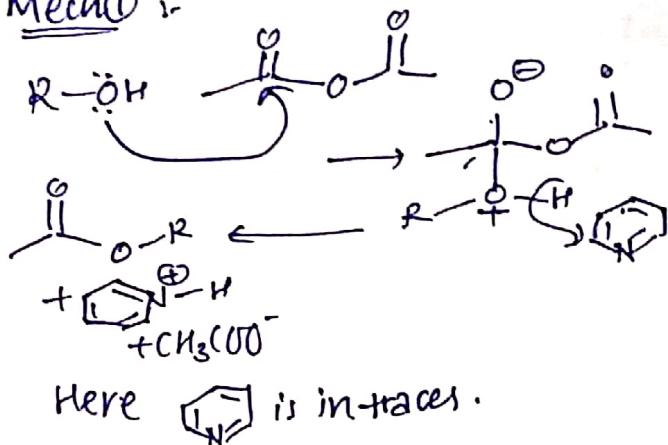
(ii) All three directly involved in acetylation / Acylation by means of CR_3COCl , $\text{CR}_3\text{COOC(O)CH}_3$.

~~To solvate leaving group~~

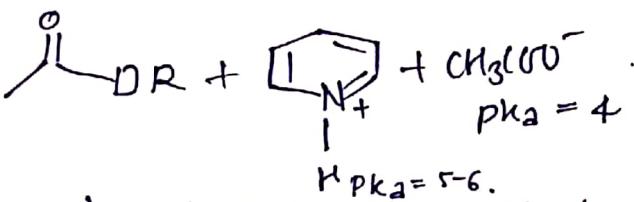
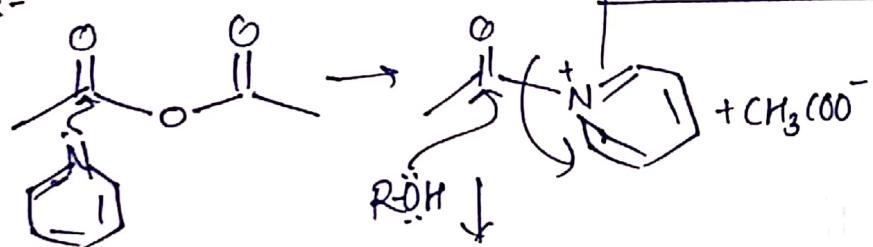
Schotten-Bauman

for -OH /  cor? \longleftrightarrow N
 for -NH₂ / May or may not

Mech① :-



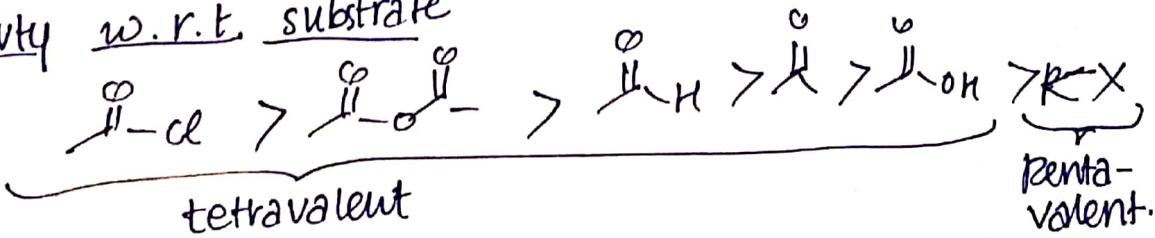
Mech② :-



Q To acylate one mole of R-OH, How many moles of (AC)₂O is required?

Ans: 1 moles

Rctvty w.r.t substrate



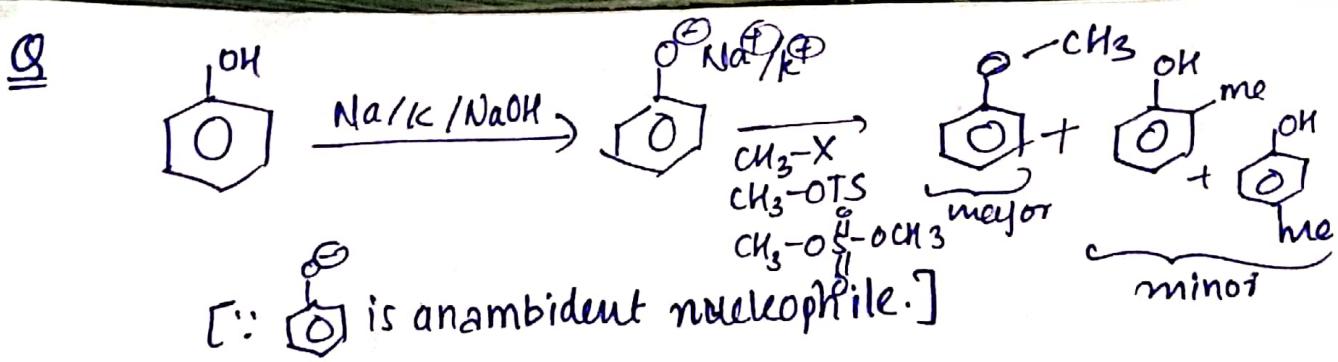
for rxn of R-X, good nucleophile is required.

Thus only R-NH₂ is alkylated.

Q How to alkylate alcohol?

→ Williamson's ether synthesis

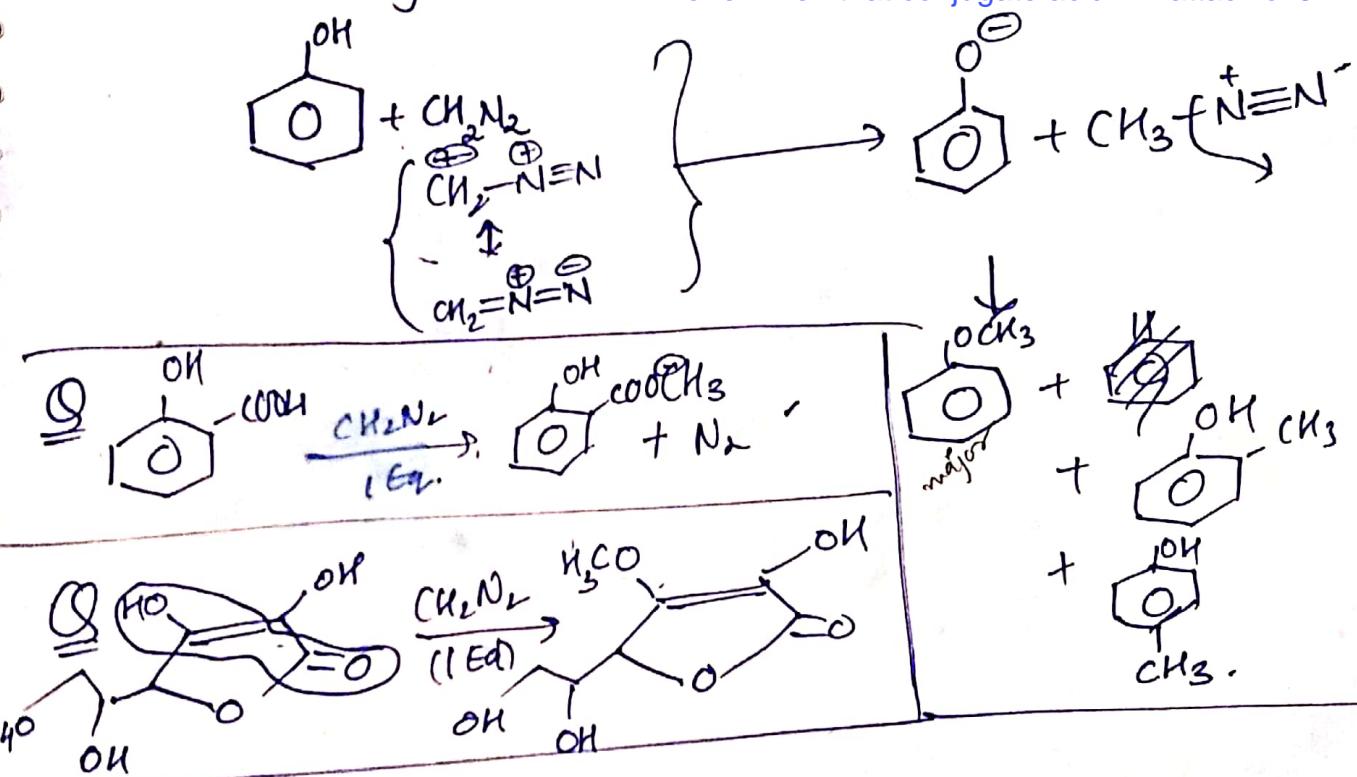
[S_N² rxn b/w alkoxide ion and alkyl halide]



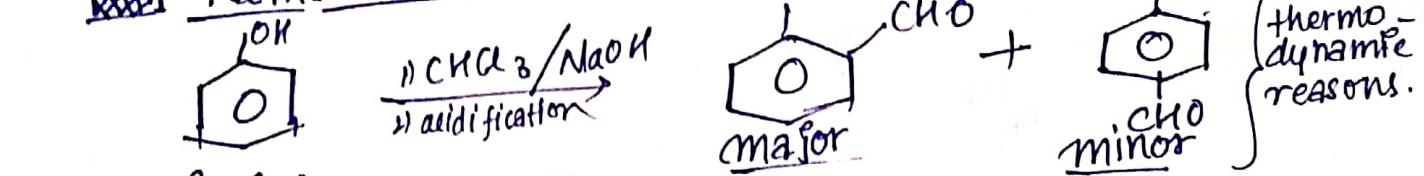
(2)

 By using CH₂N₂

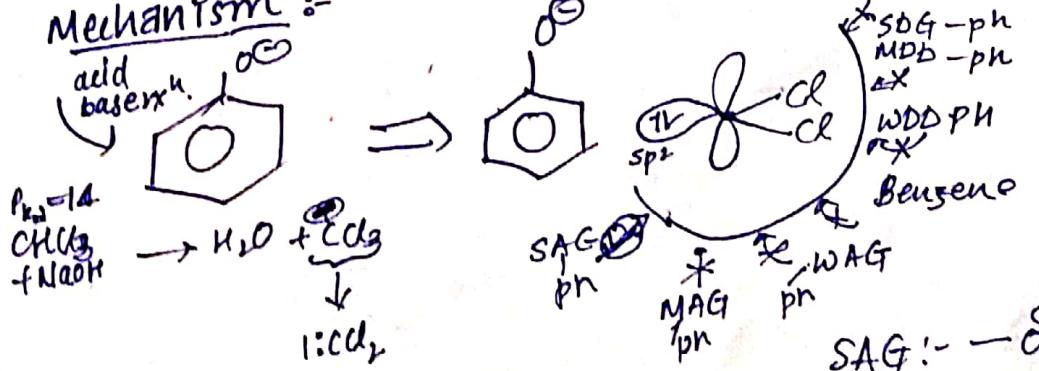
That means, first, ch₂- will abstract proton from most acidic one. Then that conjugate acid will attack ch₃n₂+



(3) Riemer Tiemann Rxⁿ



Mechanism :-

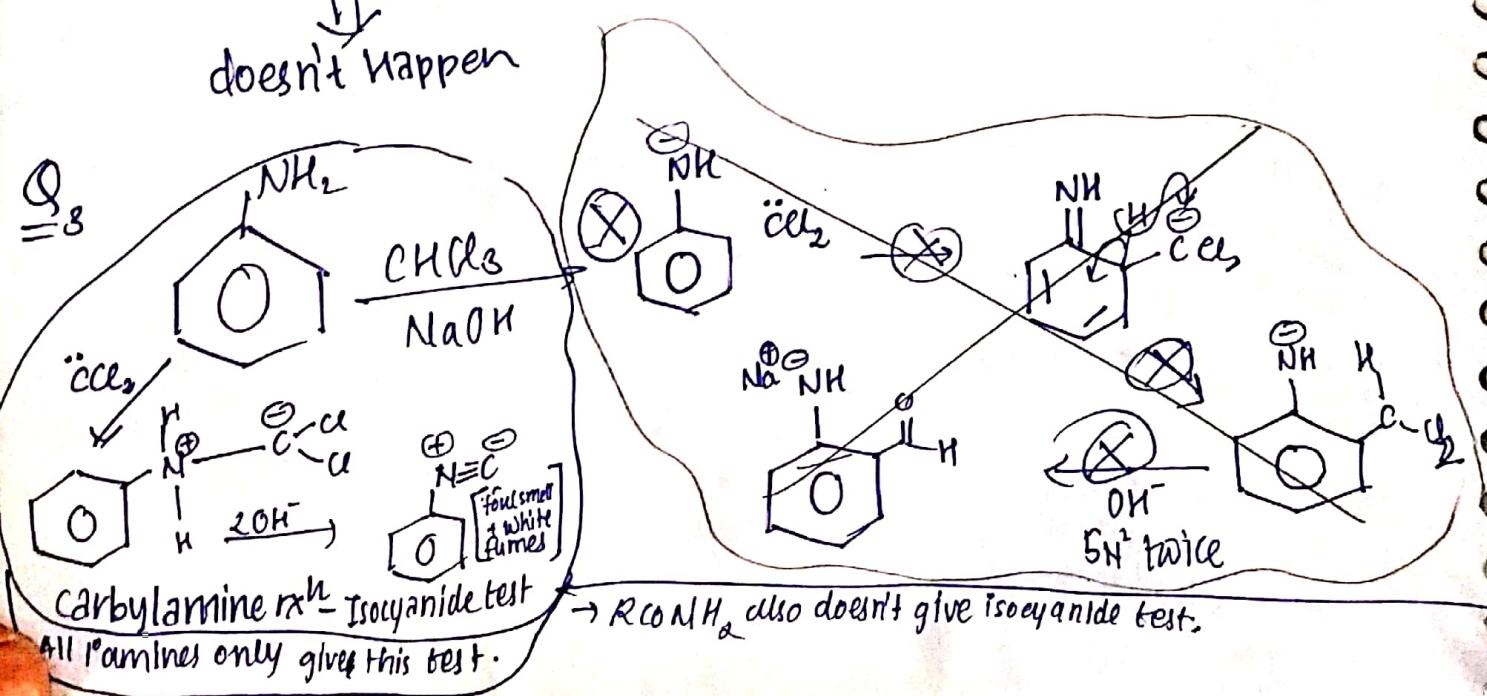
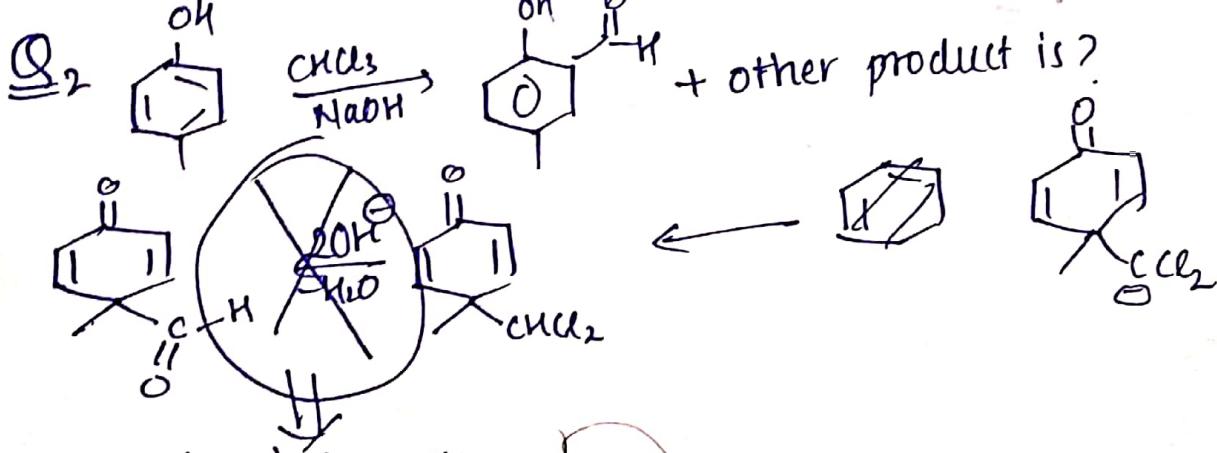
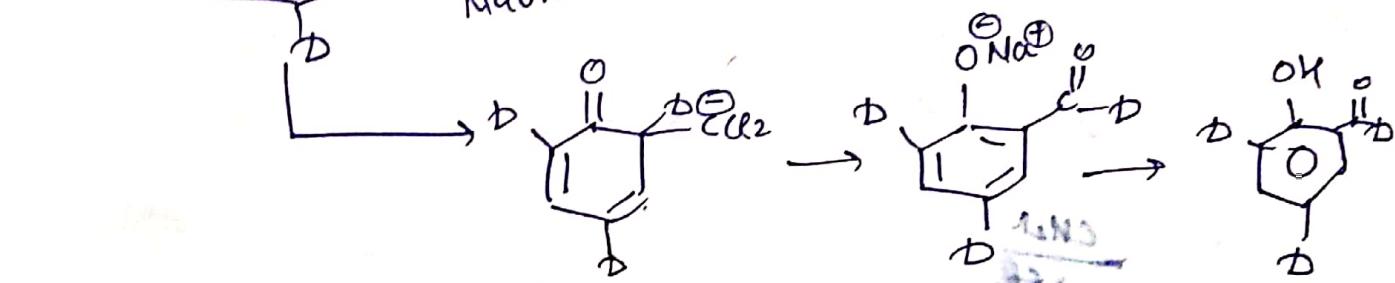
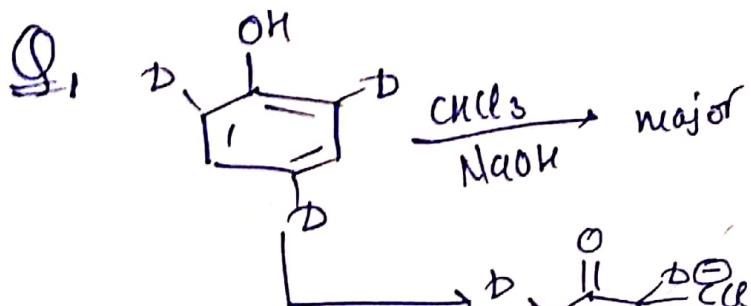
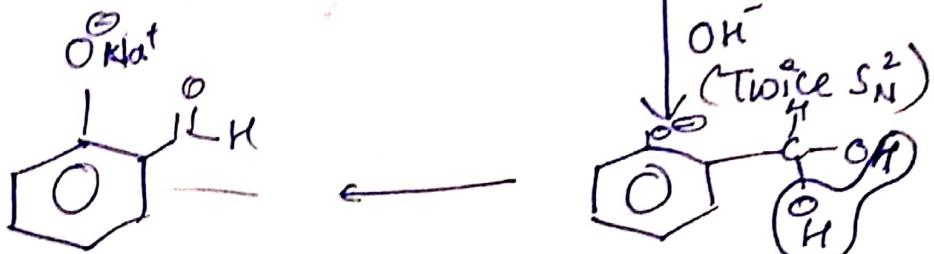


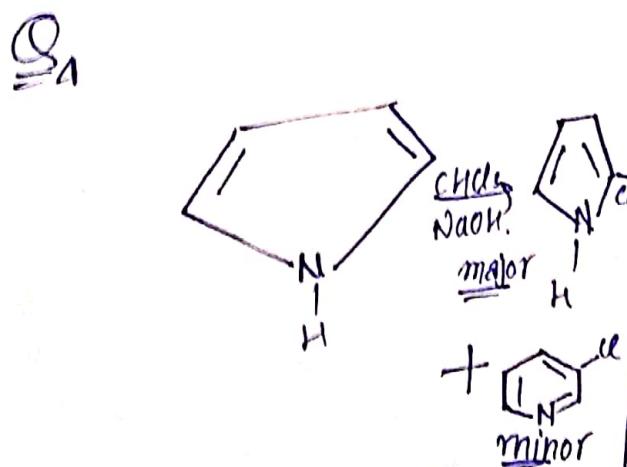
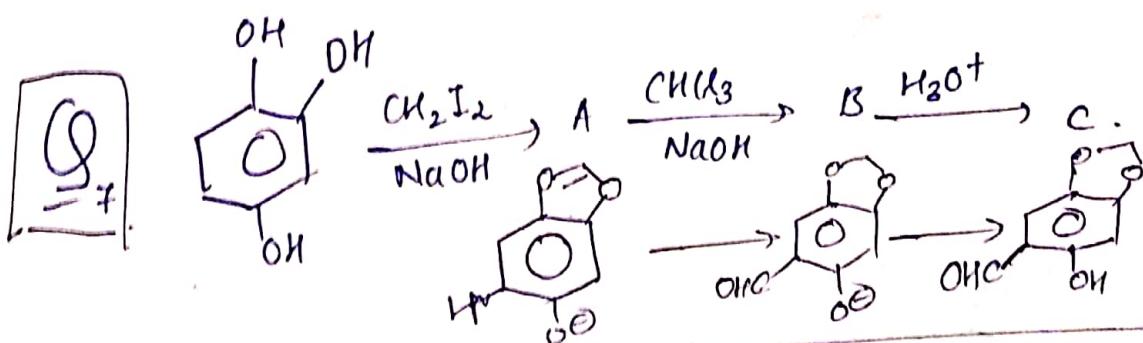
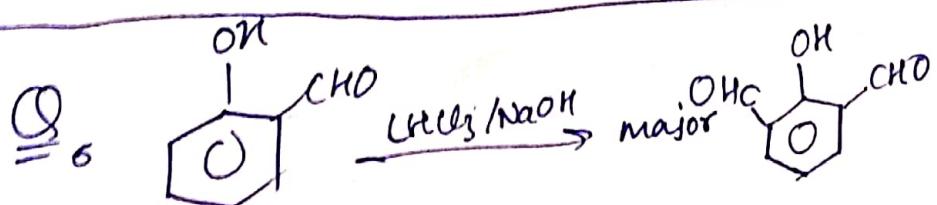
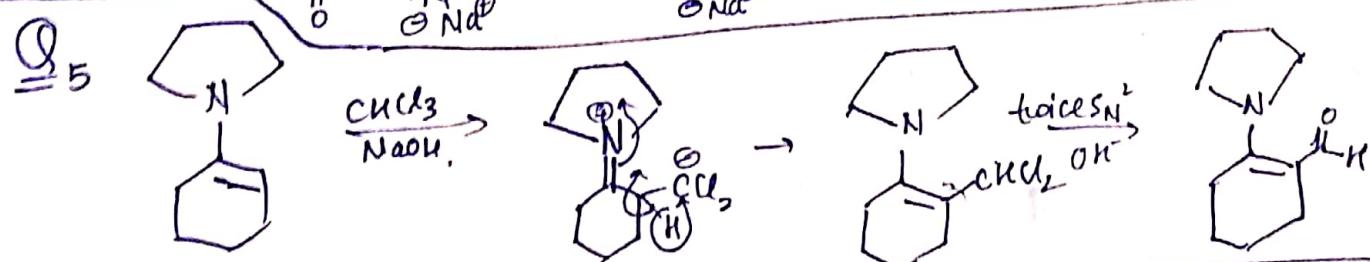
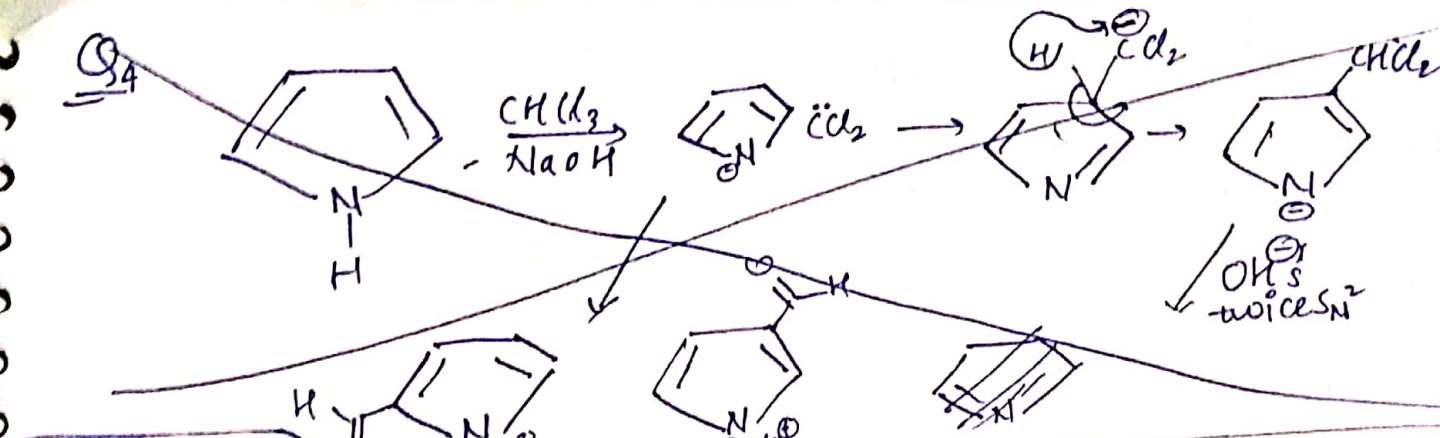
(singlet
dichloro carbene)

A hand-drawn diagram of a benzene ring. The ring has several labels: "MAG" with a crossed-out "pr" at the top-left, "WAG" with a crossed-out "pr" at the bottom-left, "SDG - ph" at the top-right, "MDD - ph" below it, "EX" below that, "WDD PH" with a crossed-out "EX" below it, and "Benzene" written vertically along the right side of the ring.

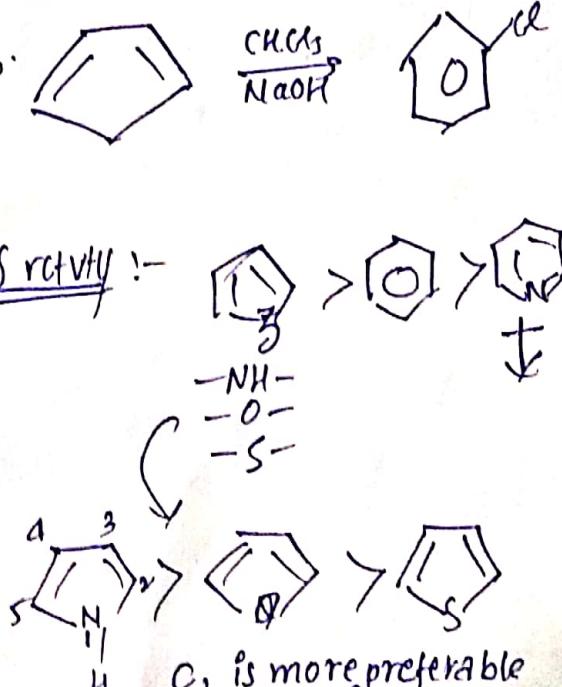
SAG: -O[⊖] > -N₂ > -NH₂ > -NH

} due to
thermo-
dynamic
reasons.

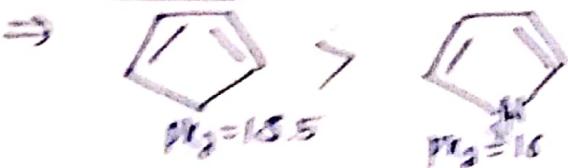




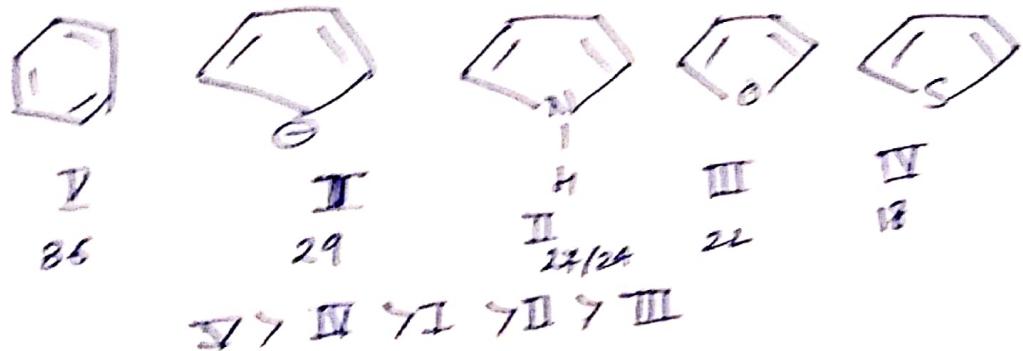
EAS rectvly :-



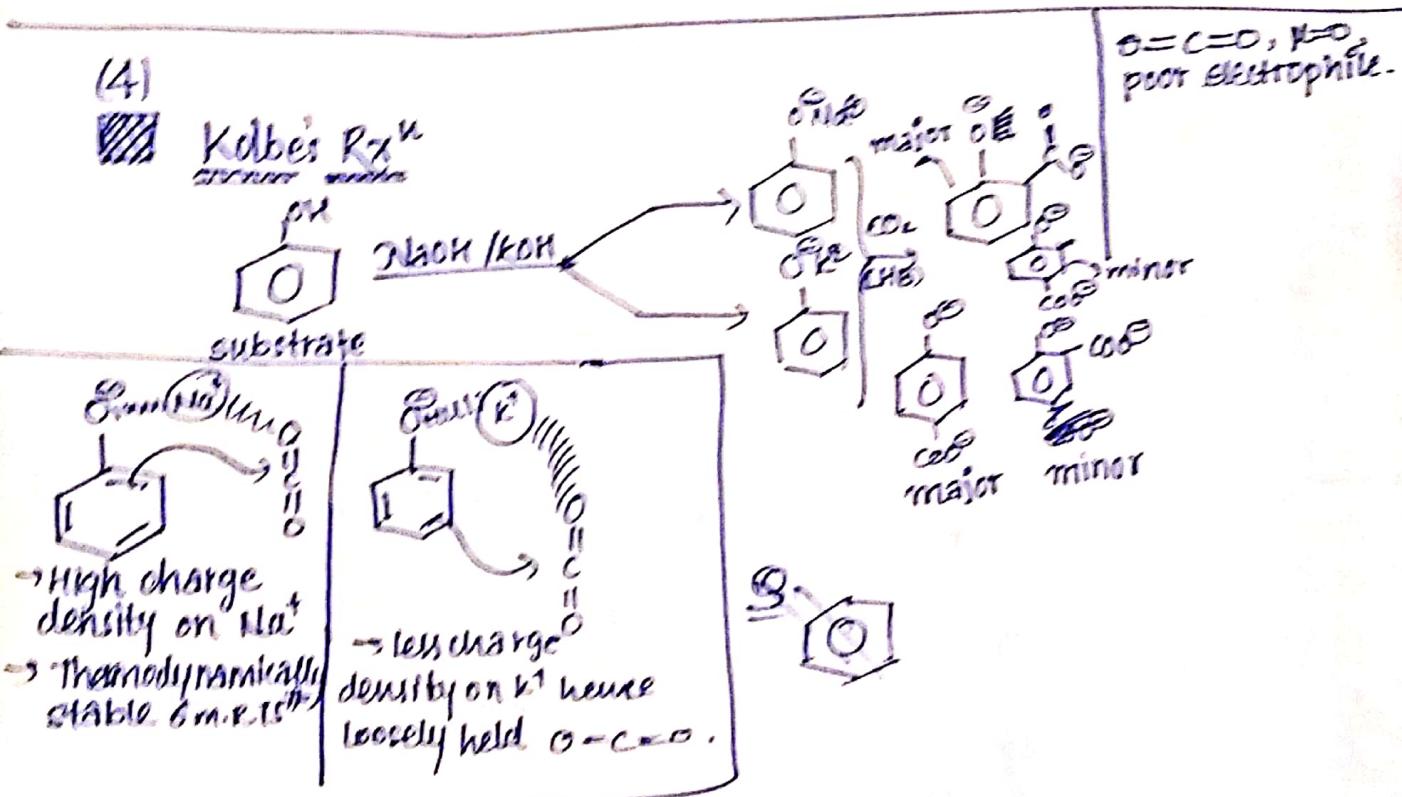
*GOC →

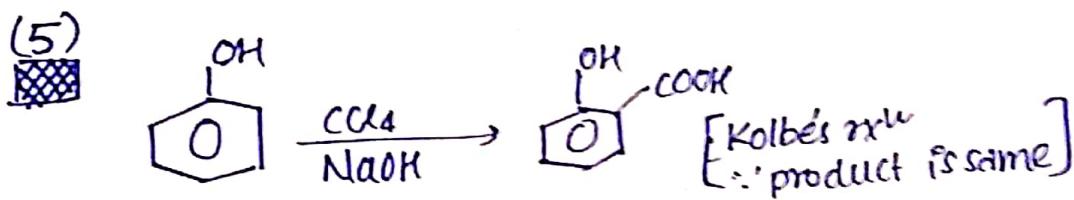
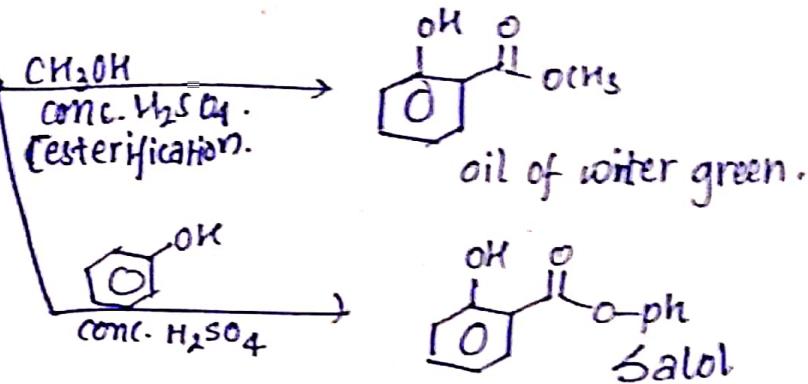
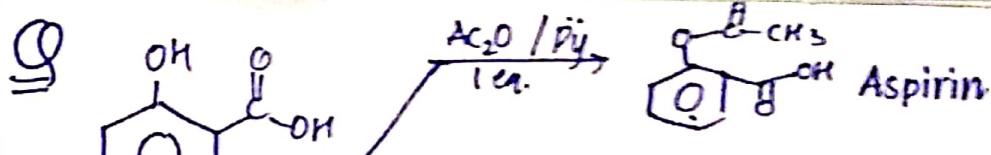


⇒ Resonance Energy order

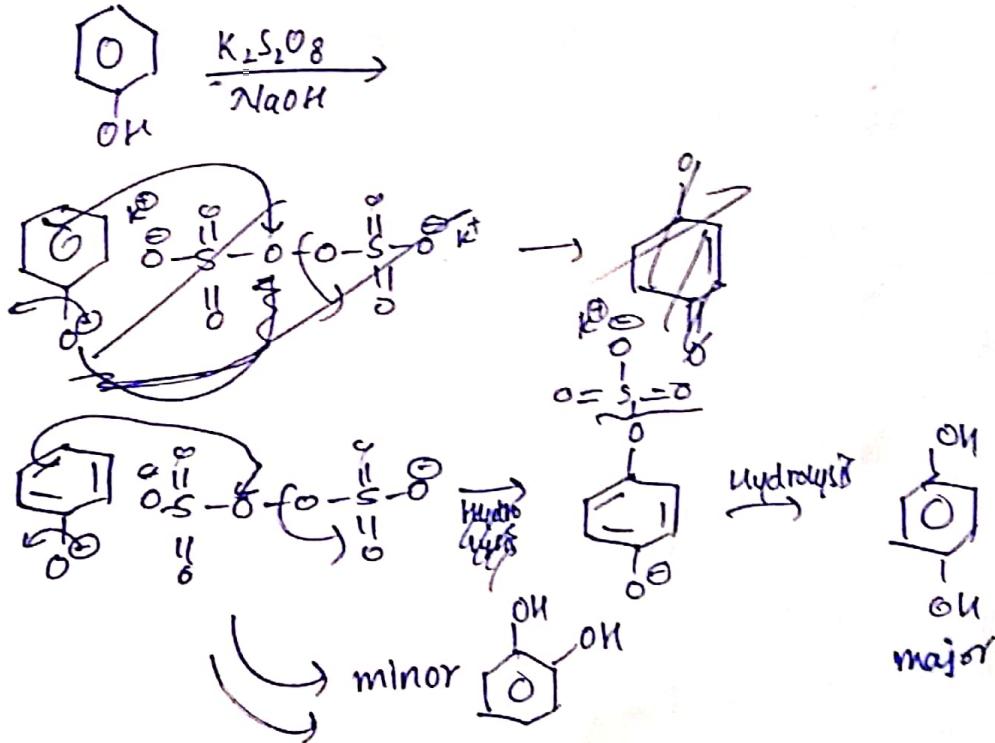


(4)



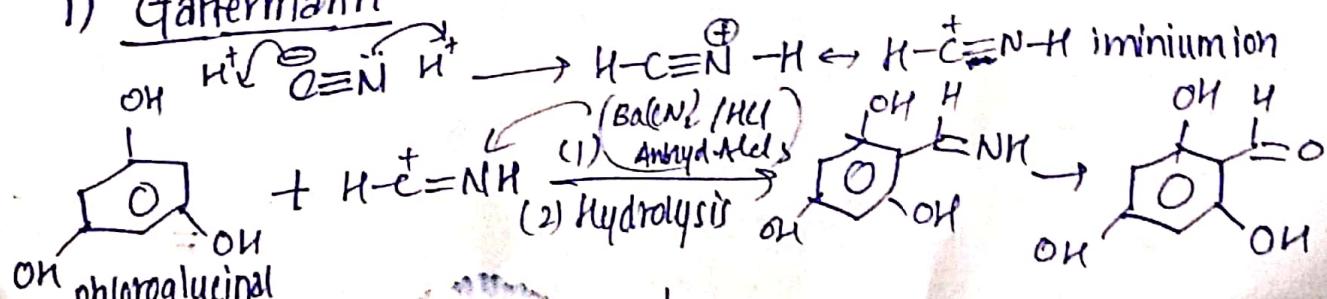


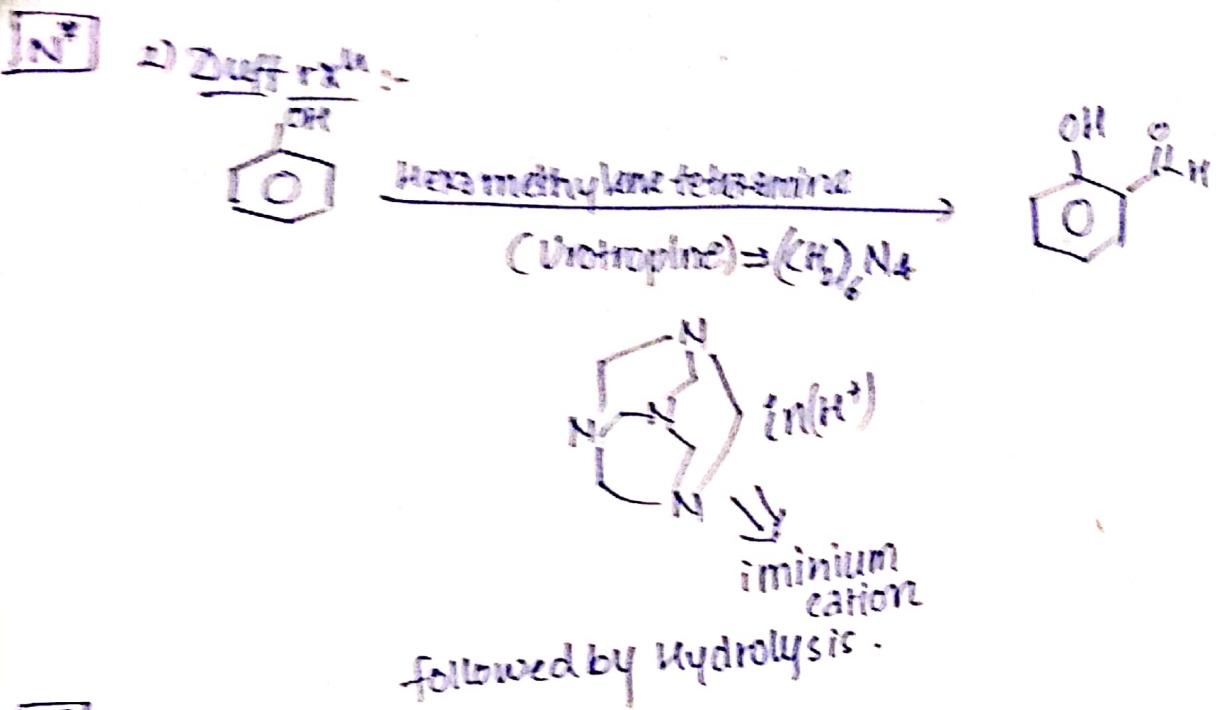
N* Elbs' rxn



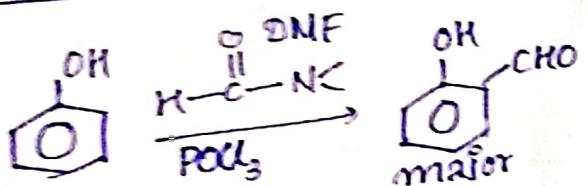
(6)
Other formylation rxns

1) Gattermann

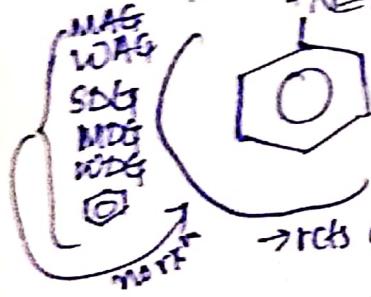




N^e 3) Vilsmeier Haak Rxⁿ:



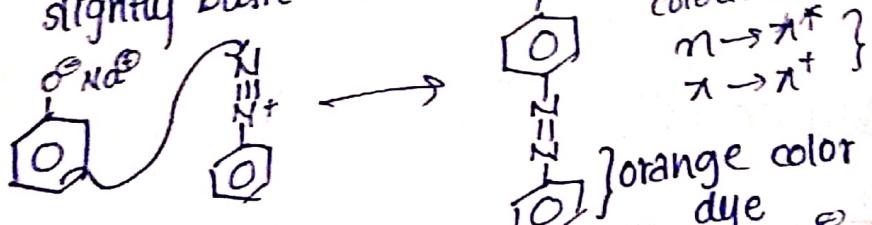
Adv * Coupling Rxⁿ (EAS)



$\xrightarrow{\text{Fe-N}_3^+$

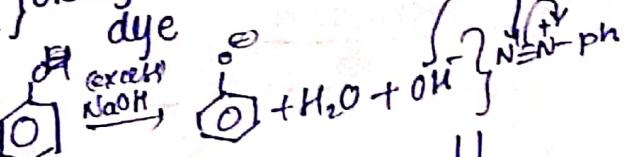
→ reacs only with strongly activating groups.

caution) p-Sub phenolic compounds gives best yield of dye (Azodye) in slightly basic medium ($pH \approx 10$)



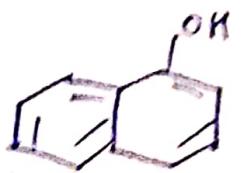
colour is due to
 $m \rightarrow \pi^*$ } conjugation
 $\pi \rightarrow \pi^+$

caution) If conc. of base is high,



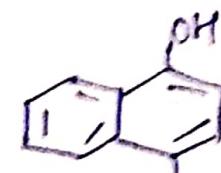
$\text{O}=\text{N}-\text{NH}-\text{Ph} \leftrightarrow \text{H}-\text{O}-\text{N}=\text{N}-\text{Ph}$
No color due to absence of extended conjugation.

Q

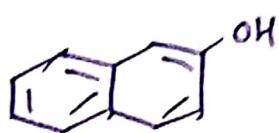


α -naphthol
1-naphthol

Ph-NHN^+
 $\text{pH} = 10.2$

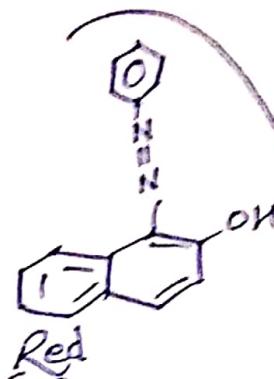


Q



β -naphthol
2-naphthol.

Ph-NHN^+
 $\text{pH} = 10.2$

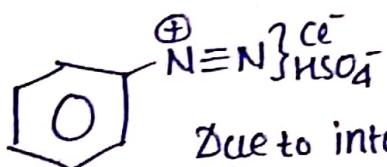


Red

Red
original Brown

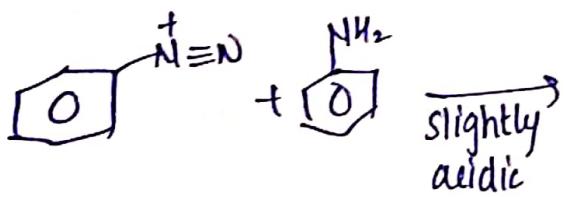
case(iii)

Anilines gives best yield of Azo dye, in slightly acidic medium.



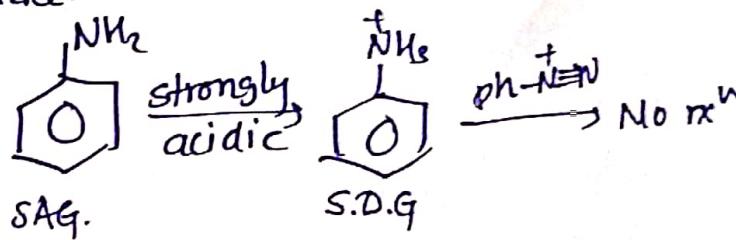
become

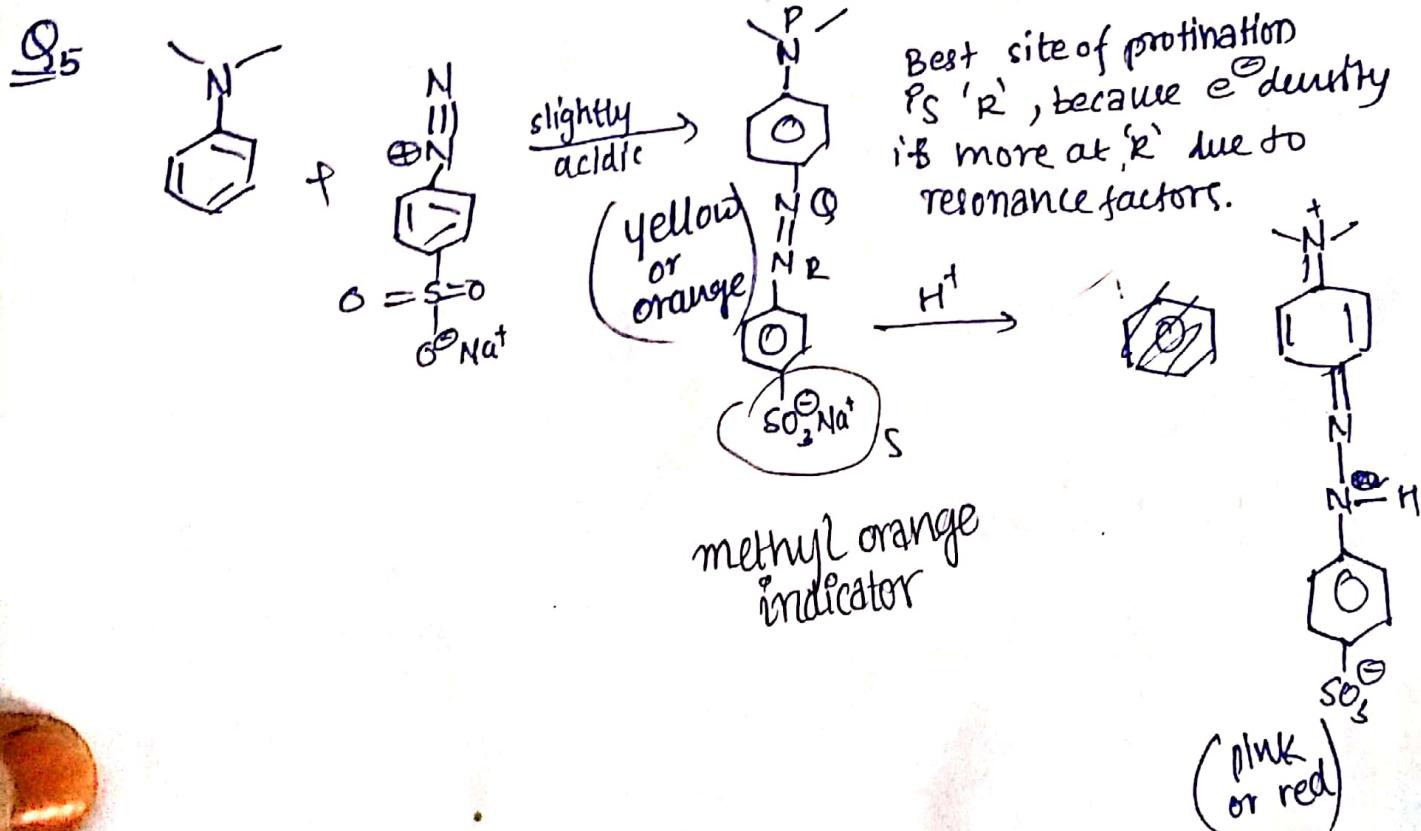
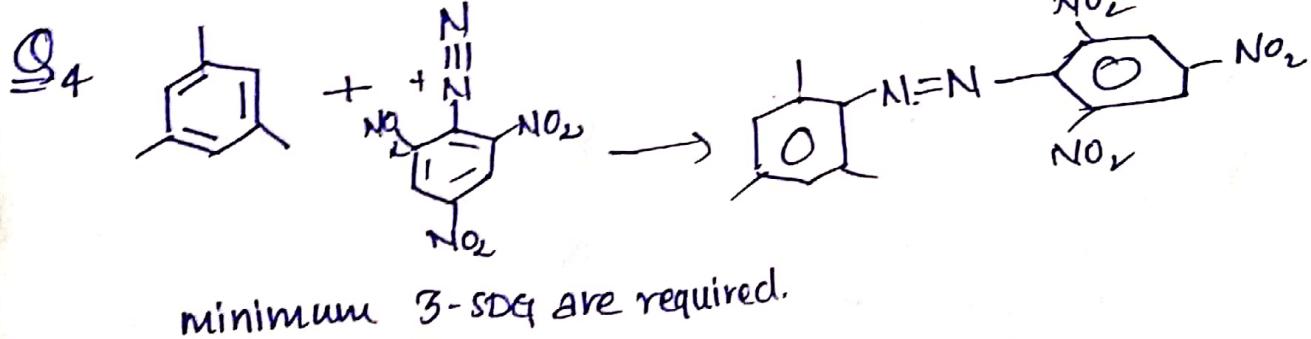
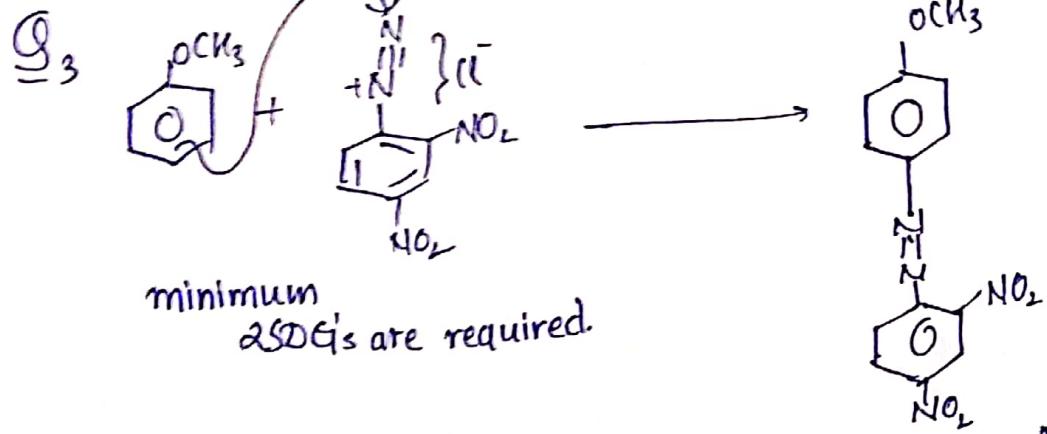
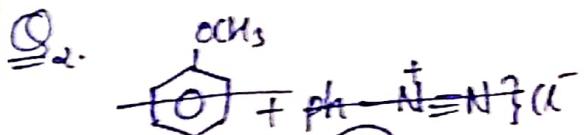
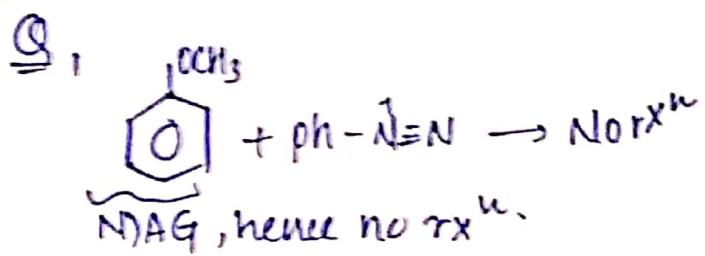
Due to interaction of $\text{N}_2^+ \{ \text{U}/\text{HSO}_4^-$, attacking of S.A.Grp, can't do its job effectively, thus in a slightly acidic medium, the π interactions are minimised giving chance to N^+ for action.



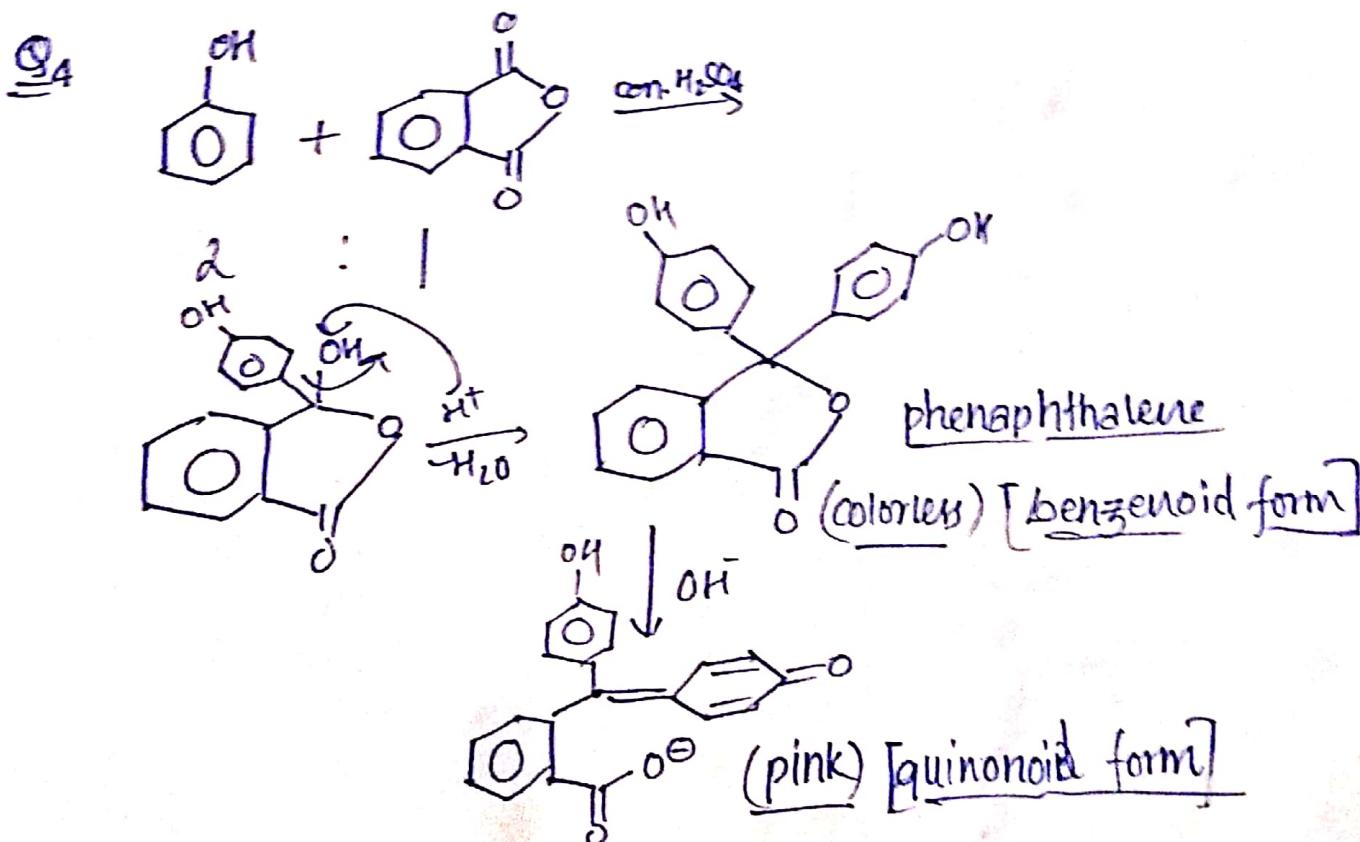
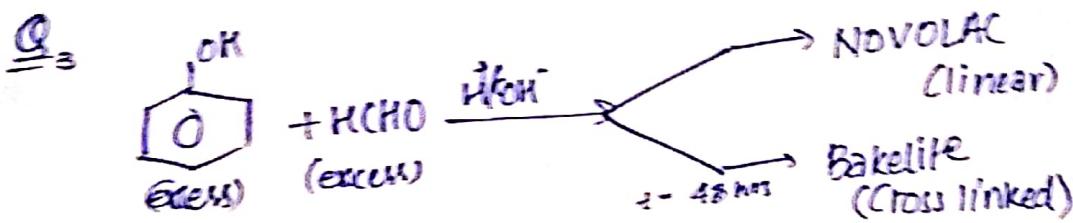
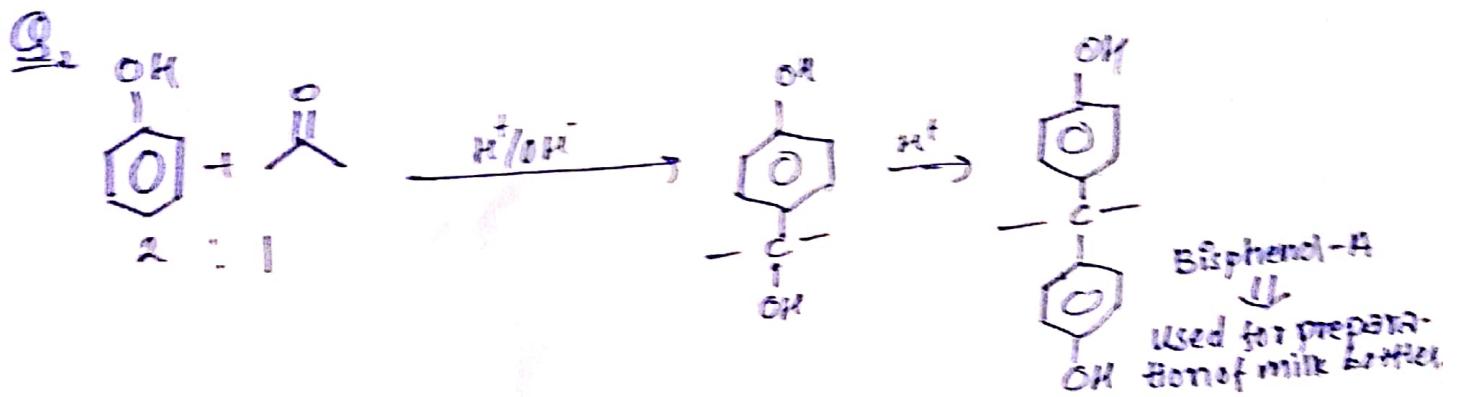
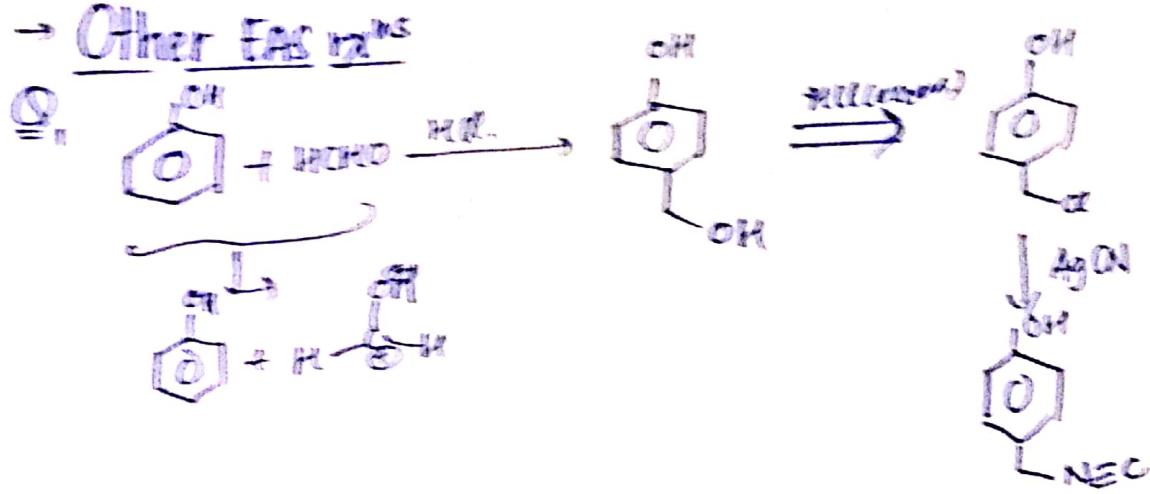
Aniline
yellow

case(iv) In strongly acidic medium dye formation doesn't take place.



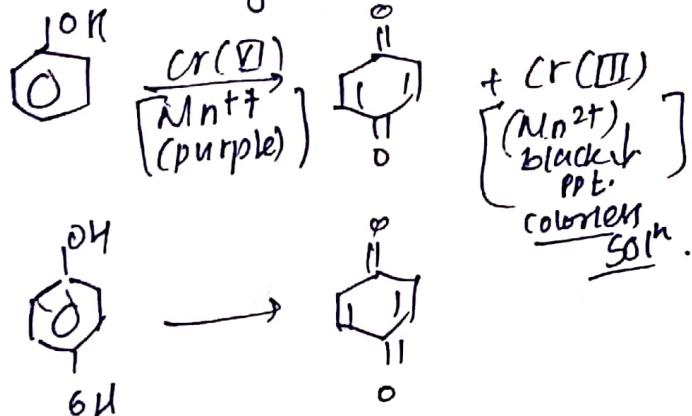


→ Other EAS rxns



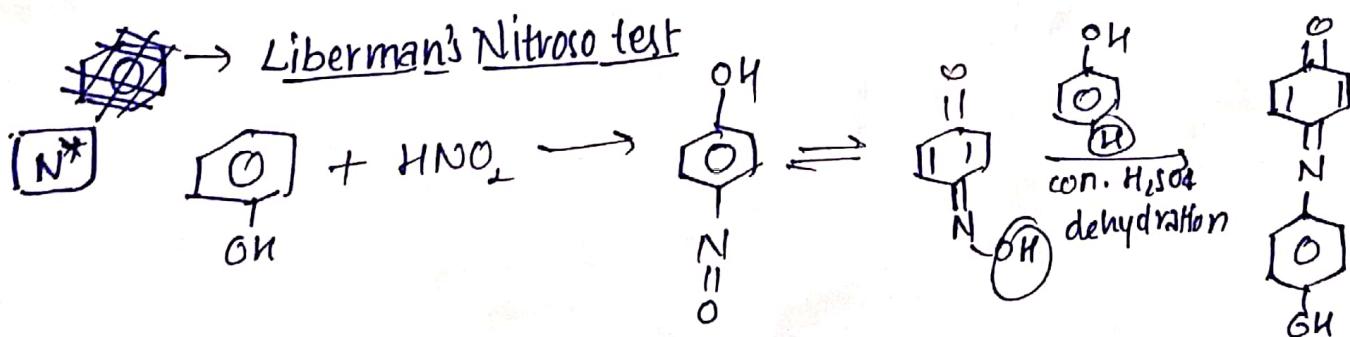
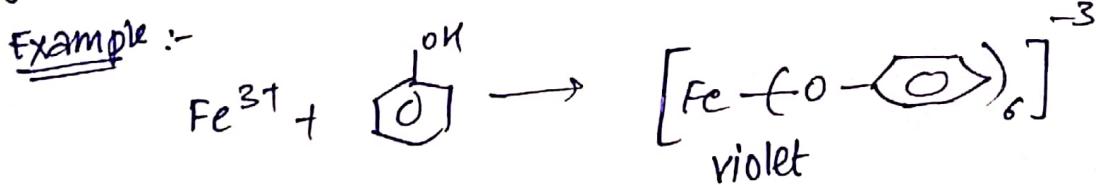
Practical Organic Chemistry related to phenols

- Phenol gives pop sound with Na.
- Turns blue litmus to red.
- Phenol gives white solid with $\text{Br}_2/\text{H}_2\text{O}$ (due to tri bromo phenol).
- Gives yellow solid with $\text{HNO}_3; \text{H}_2\text{SO}_4$ (i.e., during Nitration) due to formation of picric acid.
- Phenol turns orange color (Cr^{+6}) to Cr^{+3} (green).



→ phenol gives red coloration with CAN . (ceric $\text{NH}_4^+ \text{NO}_3^-$)

Adv.* → Not. only phenol all appreciable amounts of phenols ($\geq 5\%$) gives characteristic coloration with neutral or aq. FeCl_3 soln.



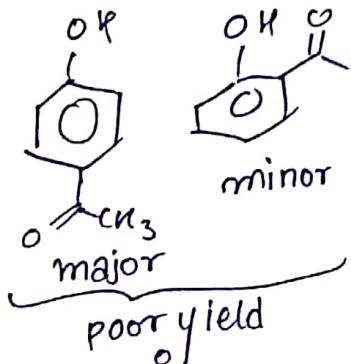
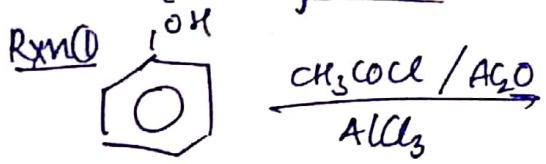
* INDOPHENOL is brown solid.

* Becomes red in ethanol, blue in NaOH.

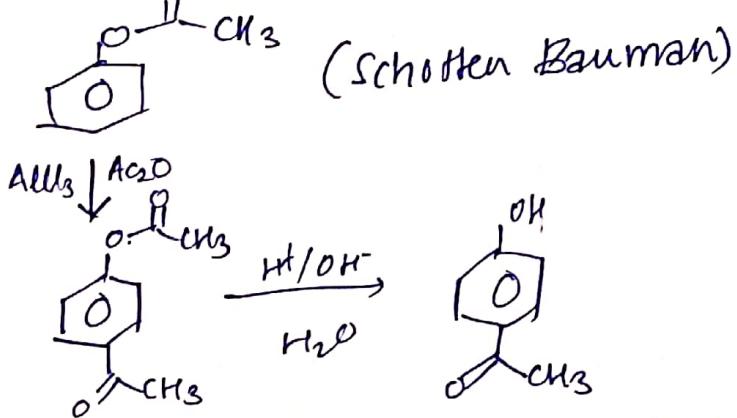
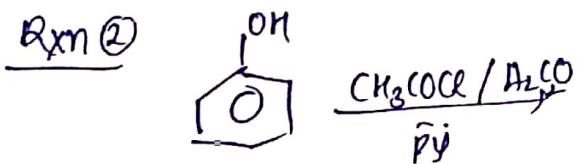
**INDOPHENOL
(Brown Solid)**

Phenols continuation

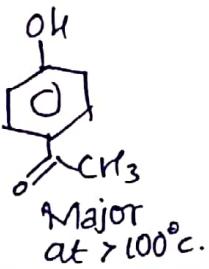
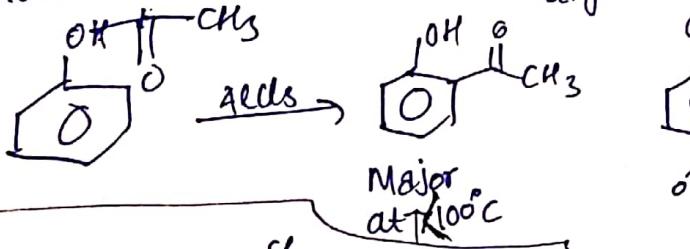
Fries Rearrangement



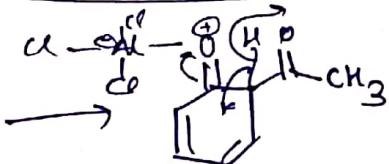
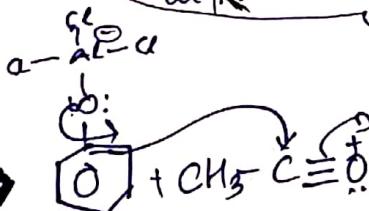
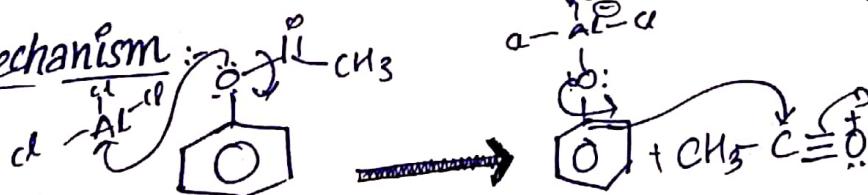
(Friedel-Crafts Acylation)



Fries rearrangement means O-acylation turns to C-acylation.
Schotten-Bauman product $\xrightarrow[\text{Friedel-Crafts reagent}]{\text{Ac2O}}$ required product.

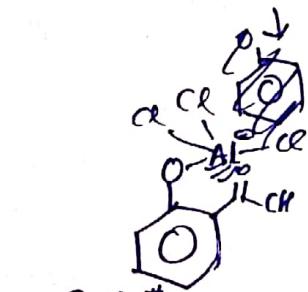


Mechanism



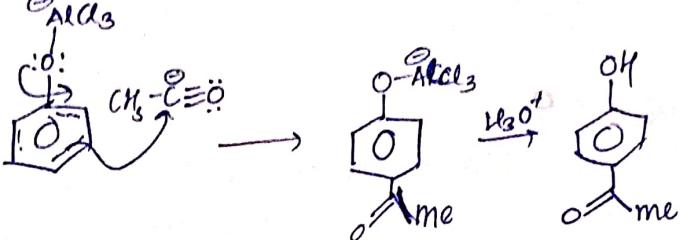
This transition occurs only because the charge gets benefit neighbouring lone pair.

Now 'O' can form further any complex and thus is ortho and para directing group.



6.7s[#]
Major at high temp. due to CHELATION
OH \downarrow Hydrolysis

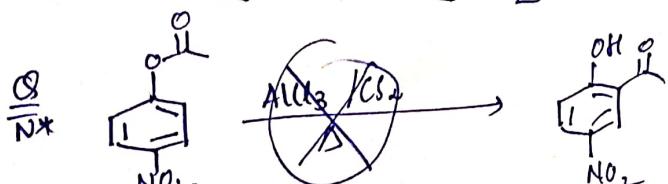
Similarly, O_1AlCl_3



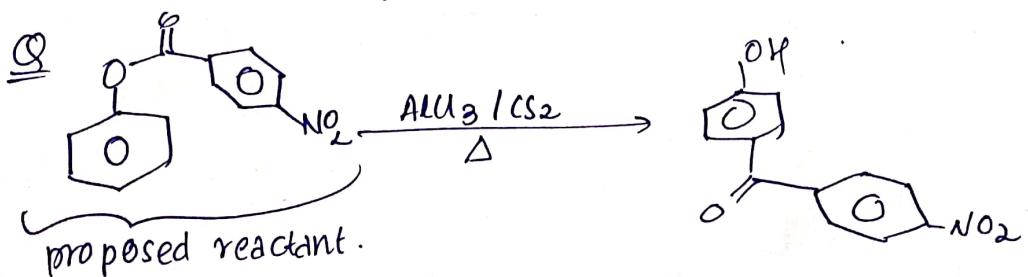
Major at <100°C

NO CHELATION

It is a type of inter molecular rearrangement. NO CHELATION.



NO_2 Because of strongly deactivating group the detached group can't enter back again.



SEE MAIN Which is fluorescein?

Ansäuerung

