AMINES

13/07/2025

- **Carbyl Amine Test**
  or Isocyanide Test –

For 1° amines (both aliphatic & aromatic)

$$R-NH_2 + CHCl_3 + 3KOH \longrightarrow R-NC + 3KCl + H_2O$$

(Foul smelling)

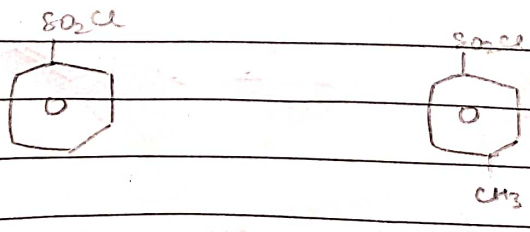
NOTE: $E\oplus$ is $:CCl_2$

- **Hoffmann – Mustard reaⁿ –** For 1° amines

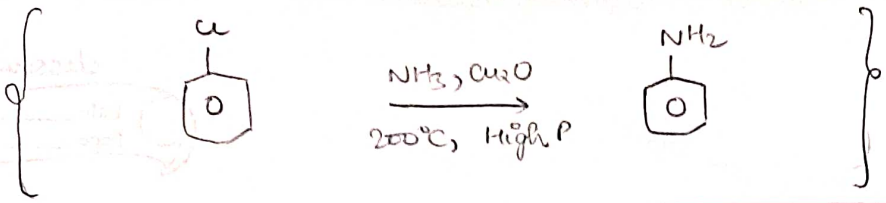
$$R-NH_2 \xrightarrow{CS_2/HgCl_2} R-N=C=S + HgS\downarrow$$

(Smells like Mustard Oil)

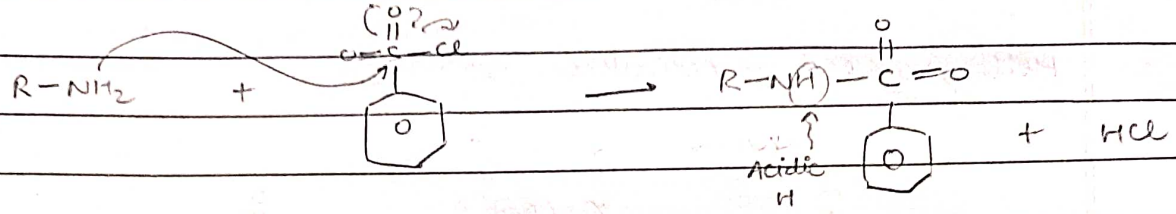
- **Hinsberg Test** – Distinguishes 1°, 2° & 3° amines



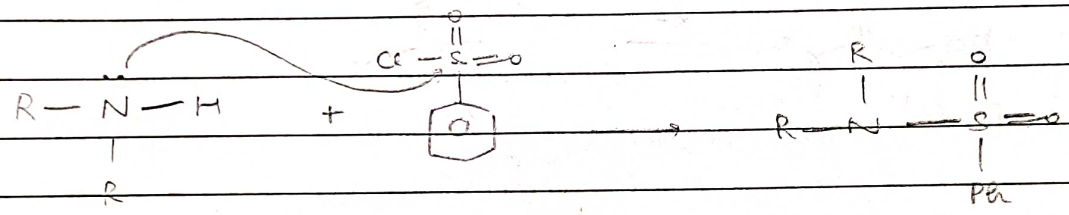
Hinsberg reagent: Old — New



classmate
Date
Page

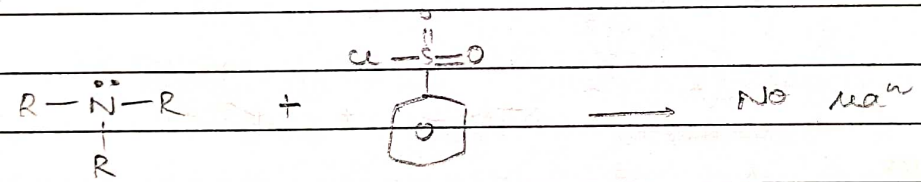
1°: 

(salt soluble in water) ← NaOH

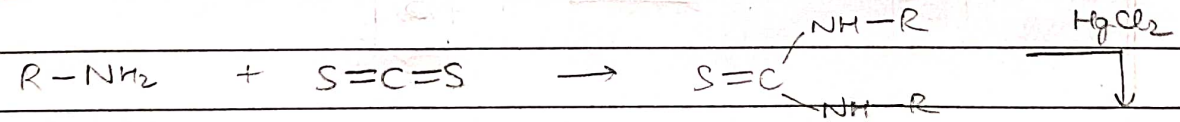
2°: 

↓ NaOH

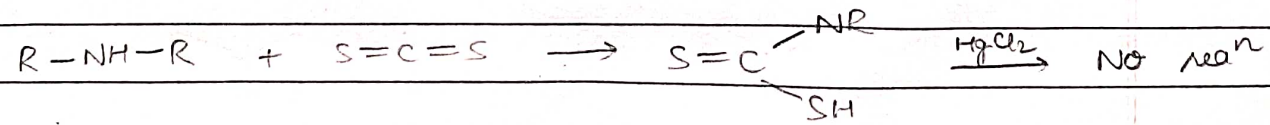
NO rea^n

3°: 

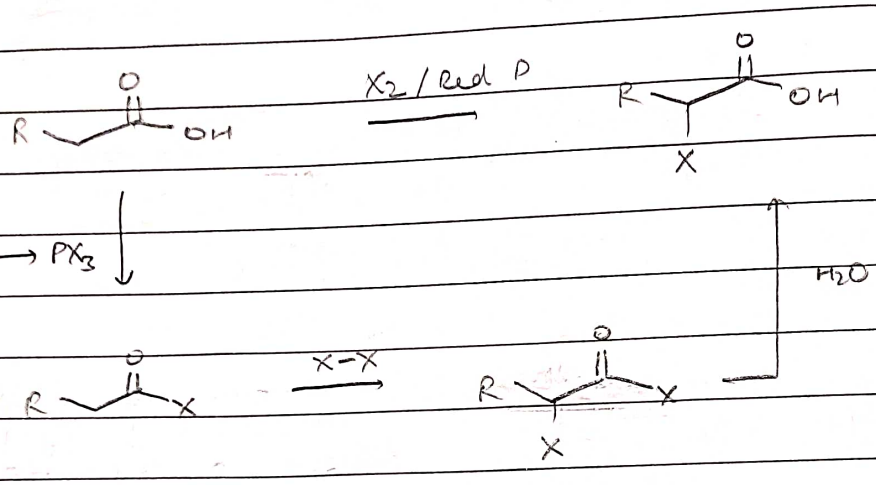
→

1°: 

2HCl + HgS↓ + R–N=C=S
(Black)

2°: 

Hell - Volhard - Zelinsky Rxn -



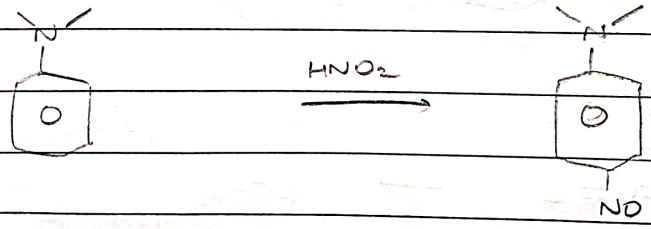
R – NC $\xrightarrow{[H]}$ R – NH

$LiAlH_4$

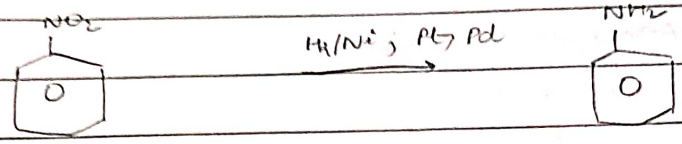
$Na - C_2H_5OH$

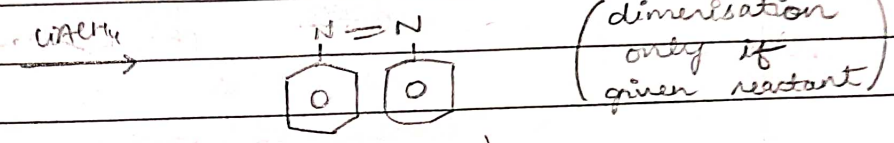
H_3O^+ R–NH$_2$ + HCOOH

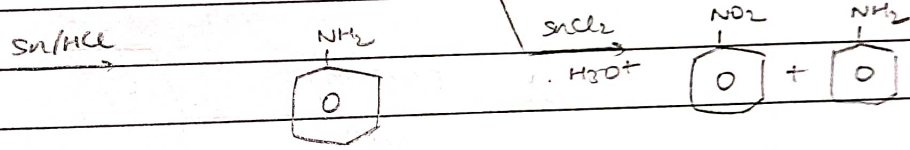
NOTE:

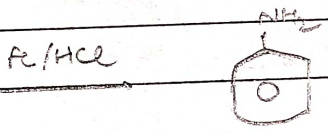


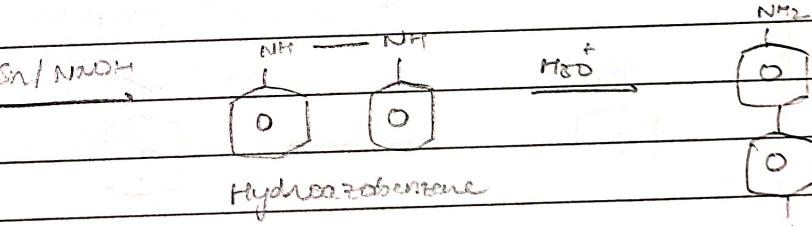
$R-NO_2 \xrightarrow[Pt/Ni \text{ or } LiAlH_4]{[H]} R-NH_2$



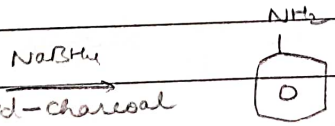


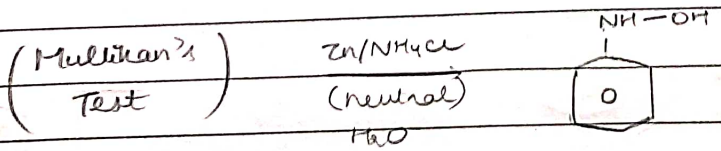






Benzidine

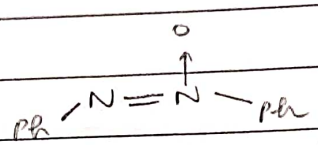




$Zn/NaOH$ → $Ph-N=N-Ph$

$MeOH$ — Azobenzene

$8[H]$

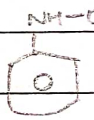
$As_2O_3/NaOH$ → 

$Na_3AsO_3 + NaOH$

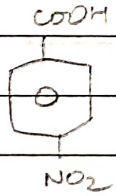
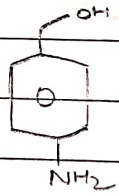
Glucose + NaOH

$Zn/NaOH$ → $Ph-NH-NH-Ph$

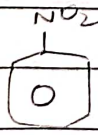
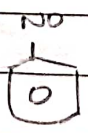
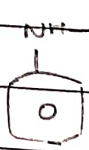
$10[H]$

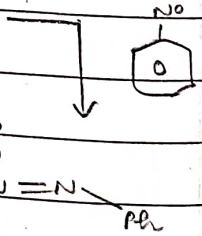
Electrolytic red^n → Strongly Acidic →  → rearrangement → 

Electrolytic red^n → Weakly Acidic → 

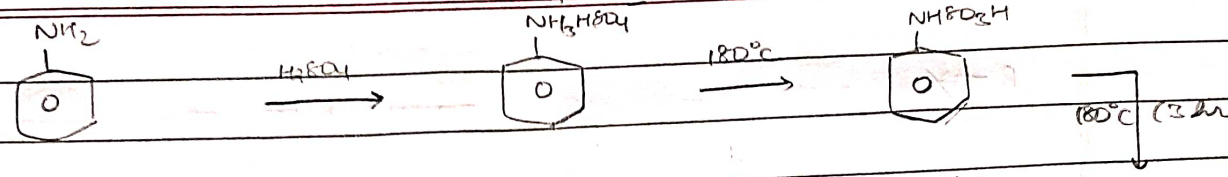
 $\xrightarrow{LiAlH_4}$ 

Mechanism

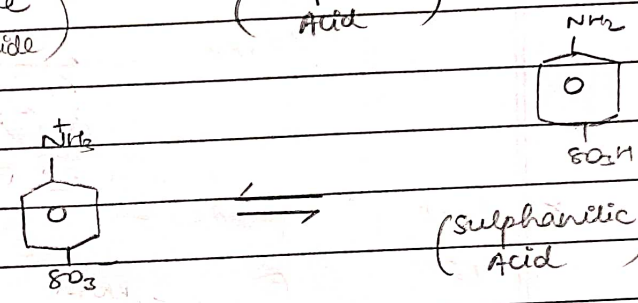
 $\xrightarrow[-[H_2O]]{2[H]}$  $\xrightarrow{2[H]}$ 



$Ph-NH-NH-Ph \xleftarrow{[H]} Ph-N=N-Ph \xleftarrow{[H]}$

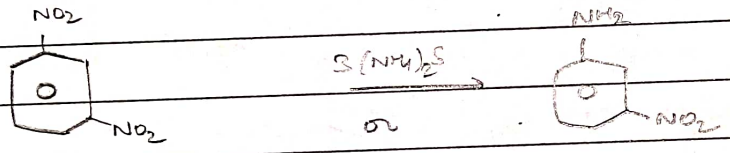


(Aniline sulphide) (Sulphanic Acid)



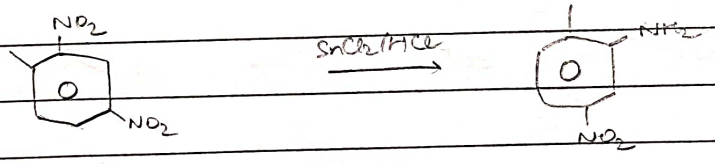
(Sulphanilic Acid)

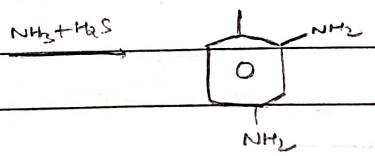
Zwitter ion
(acts as buffer)
(dipolar ion)

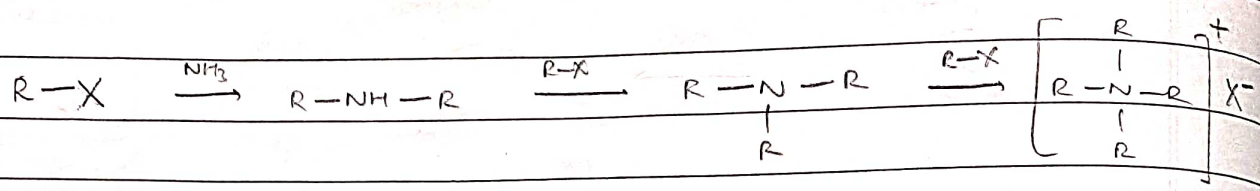


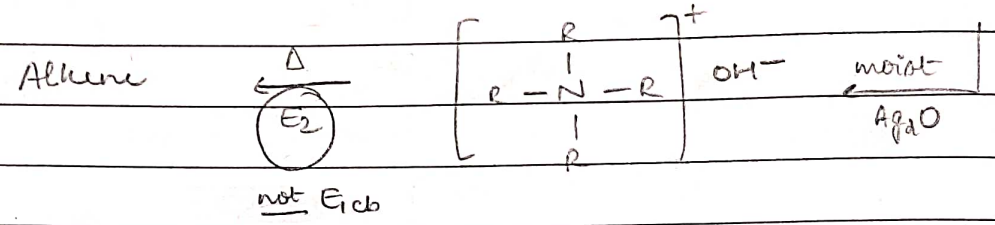
$+ 6NH_3 + 3H_2O + 3S$

~~NH_4SH~~
~~$H_2S + NH_3$~~
~~NO_2S_2~~



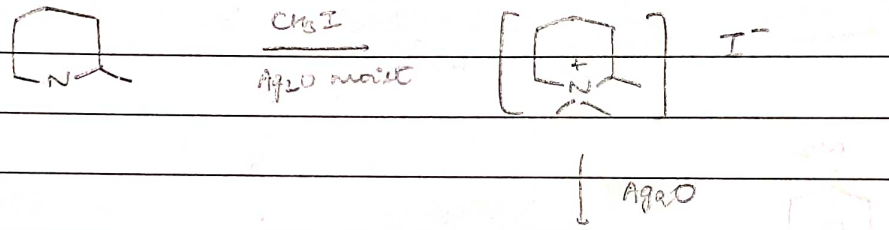




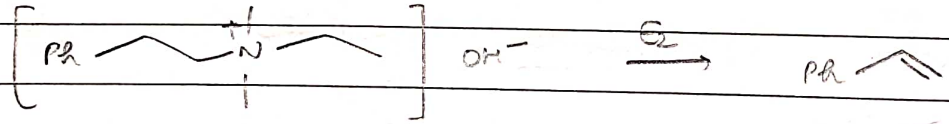


* But, product formed based on stability of $C^{\ominus}$, even though it is not formed

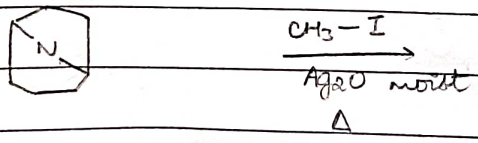
eg 1.



2.



Q.

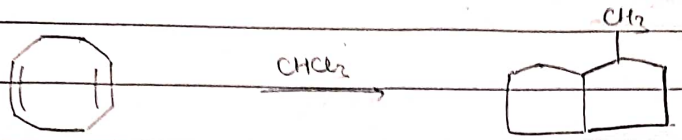


A.

[* only for AITS]

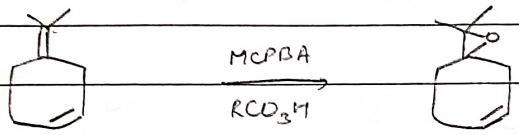
MISC REAⁿ's

1.

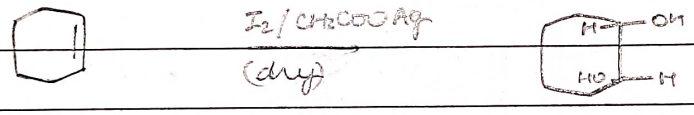


2. $R-NC \xrightarrow{Zn-Hg/HCl} R-NH-CH_3$

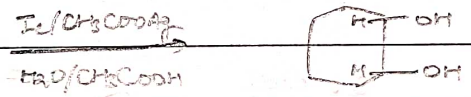
3.



4.

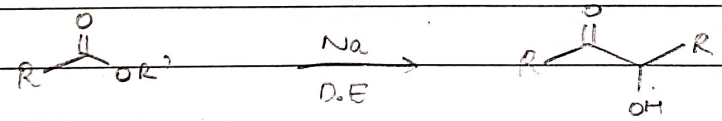


(Anti° addⁿ)

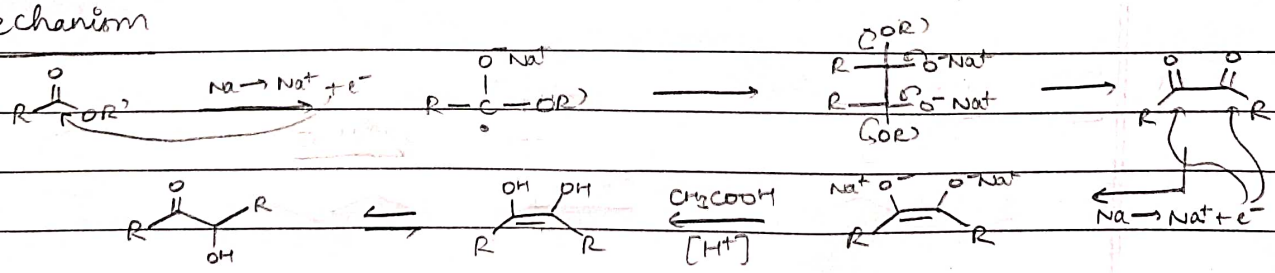


(Syn addⁿ)

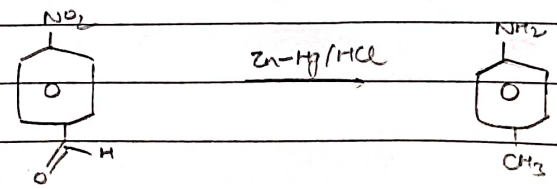
5.



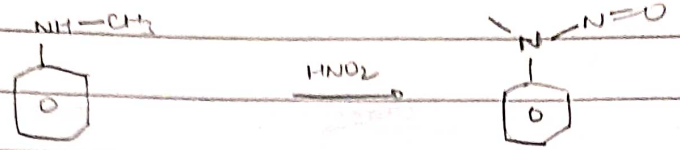
Mechanism



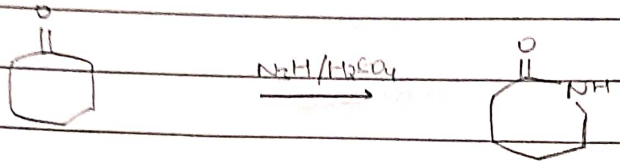
6.



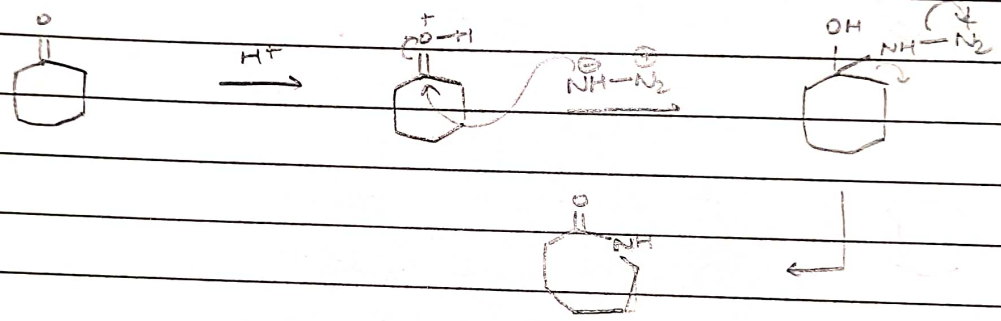
7.



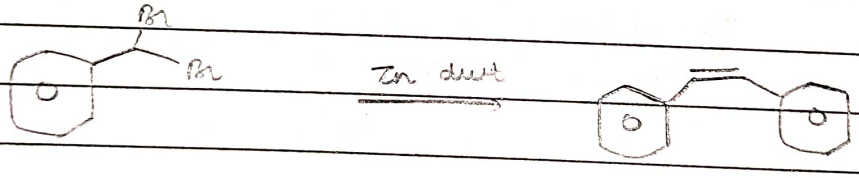
8



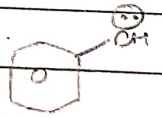
Mechanism



9.

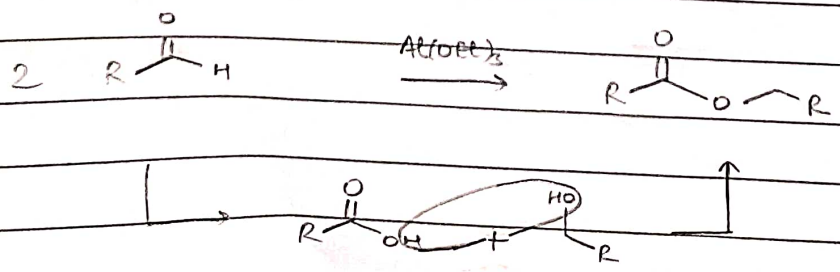


$Zn \rightarrow Zn^{2+} + 2e^-$



(Carbene)

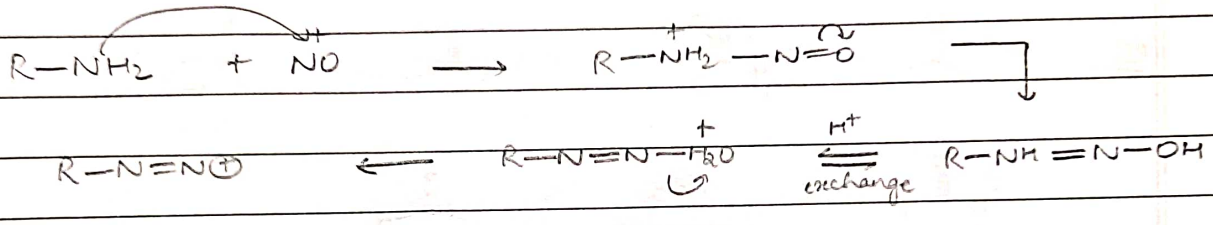
10. Tischenko reaction



11. Tilden Rxn

$$R-NH_2 \xrightarrow{NOCl} R-Cl$$

Mechanism

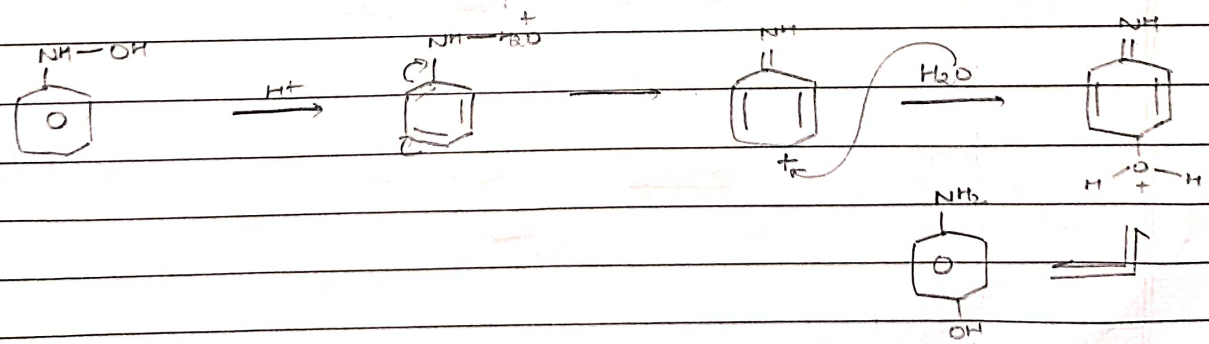


12. Raney Ni

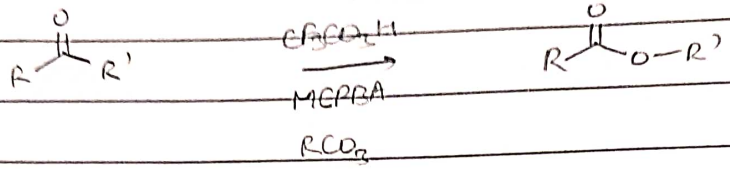
$$Ni\text{-}Al + NaOH \longrightarrow Al(OH)_3 + Ni^{\circ}\ (Powder)$$

(Raney Ni°)

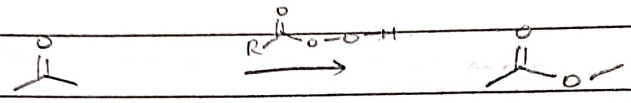
12.

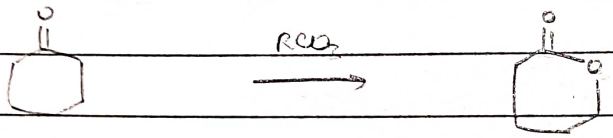


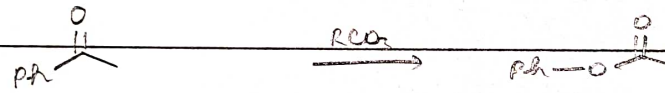
14. Bayer – Villiger Rearrangement



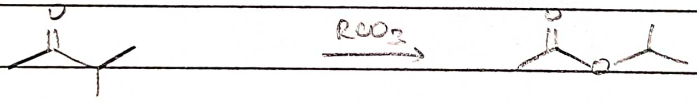
Eg

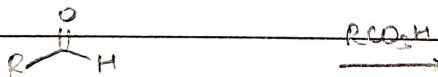




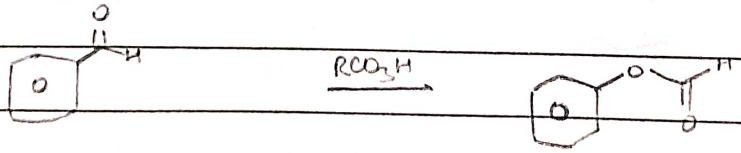


(O or R group whose migrating tendency is greater)

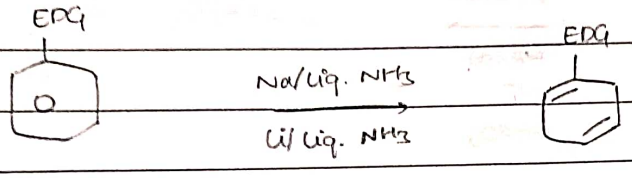


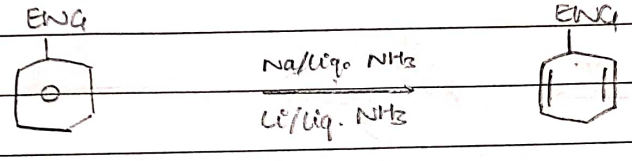


No rxn

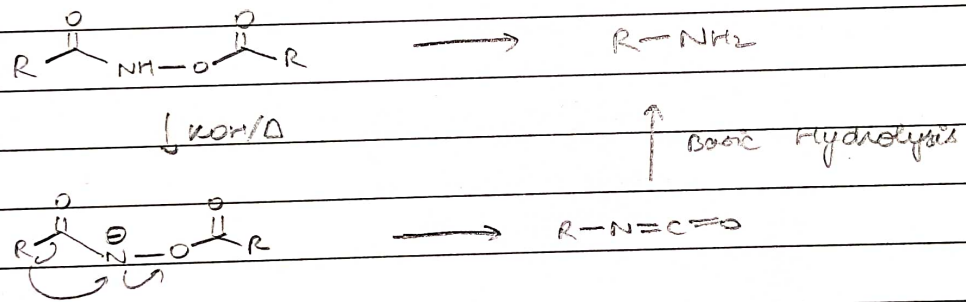


15. Birch red^{n}

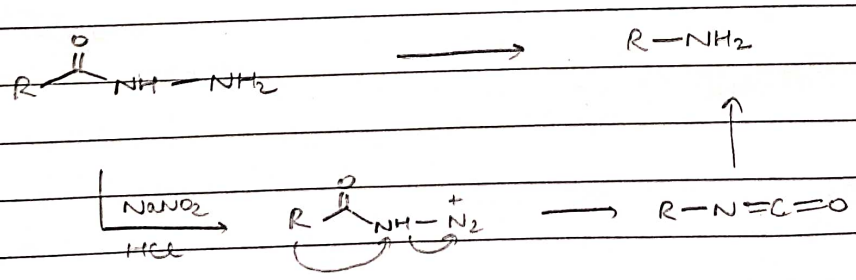




16. Lossen red^{n}



17. Curtis red^{n}



18. Schmidt rxn