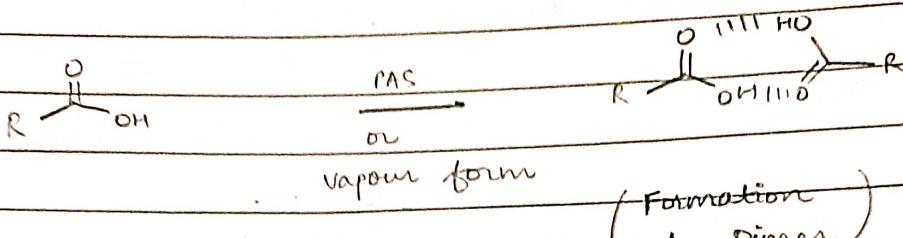
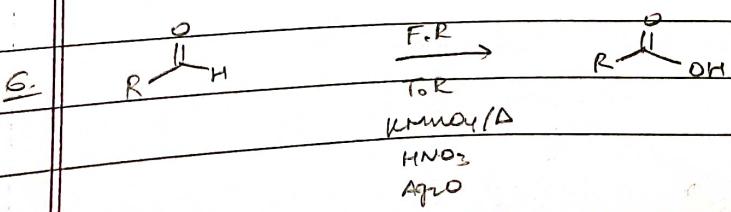
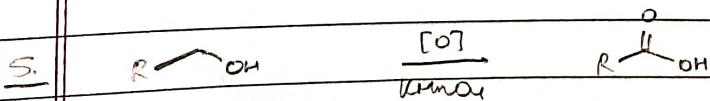
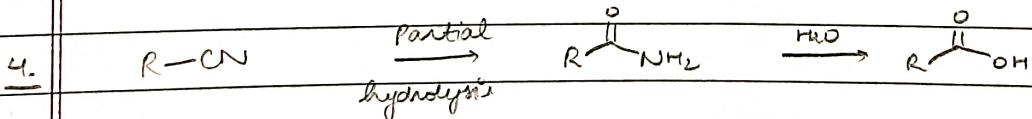
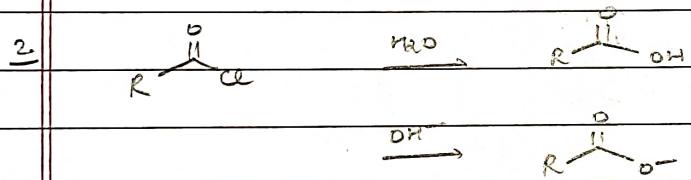
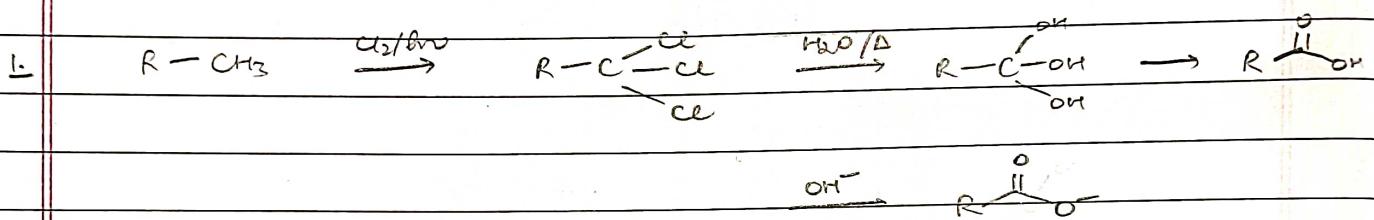
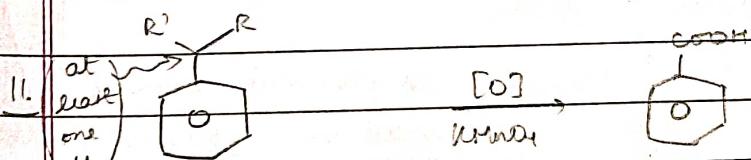
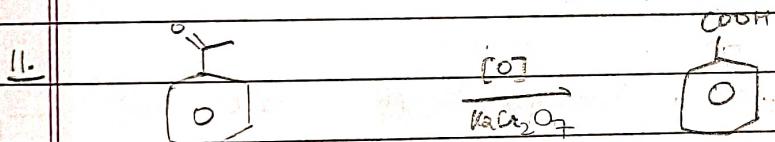
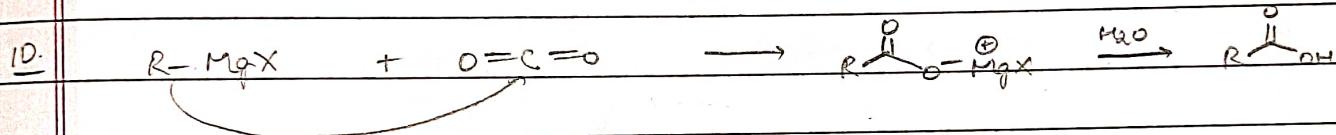
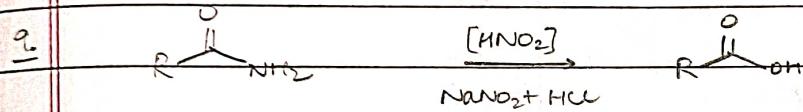
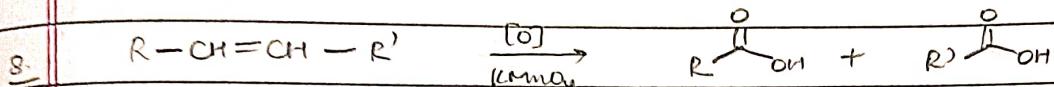
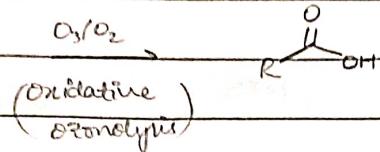


11/07/2022

CARBOXYLIC ACIDS

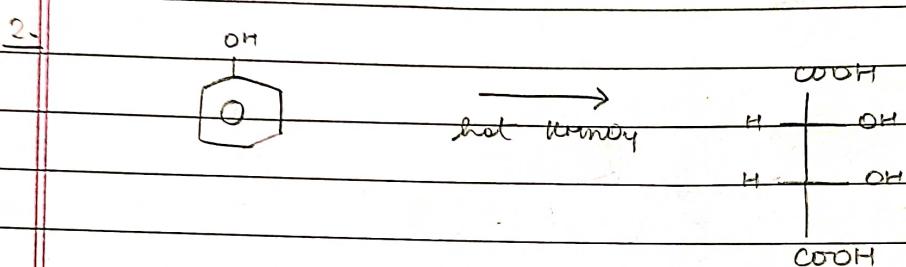
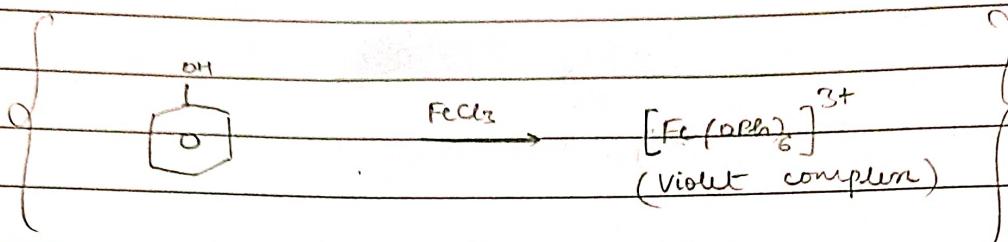
AND ITS DERIVATIVES

PREPⁿ



NOTE:

1. If any comp. give colouration with neutral FeCl_3 , it is enol or phenol. (usually violet)



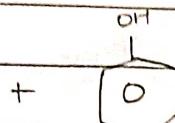
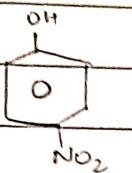
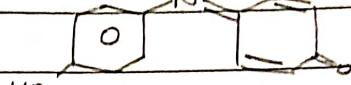
→ Detection of Phenolic Group

(1) Litmus test - Colour changes to red if liq. or crystal of comp. placed on moist blue litmus paper.

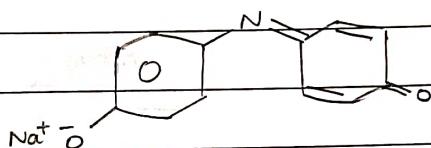
(2) Neutral FeCl_3 test - If colouration observed on reacⁿ with neutral FeCl_3 , comp. is enol or phenol (usually purple, blue or green)

(3) Liebermann's test - Green or Blue colouration test on reacⁿ with NaNO_2 & 1ml conc. H_2SO_4

If solⁿ poured into excess water → Red solⁿ
further excess NaOH → Blue/Green solⁿ

 $\xrightarrow{\text{HNO}_3}$  \longrightarrow 

indophenol (red)



indophenol anion (Blue)

→ Test for Alcohol

① CAN Test - 1° & 2° Aliphatic alcohol give

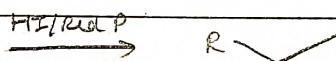
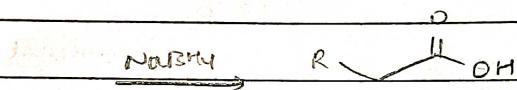
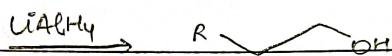
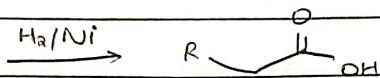
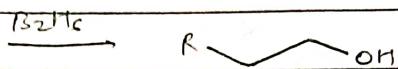
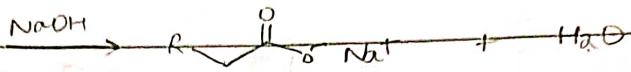
(Ceric
Ammonium
Nitrate)

→ red color on reacⁿ with CAN.

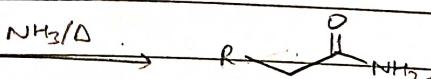
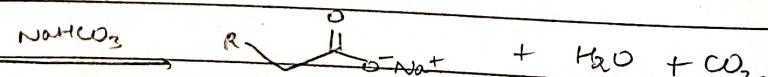
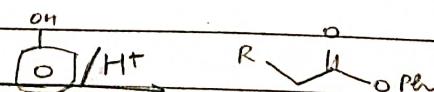
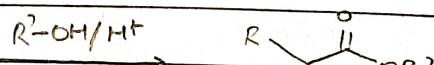
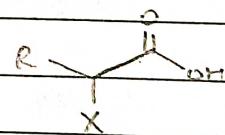
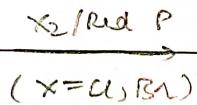
3° Aliphatic alcohol do not give CAN test.

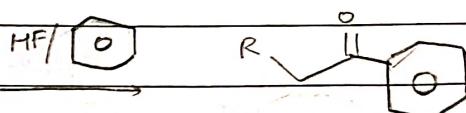
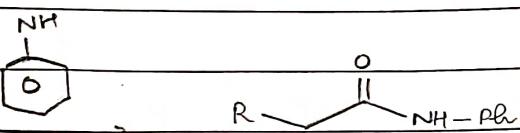
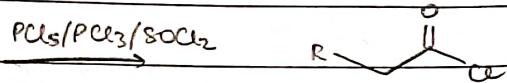
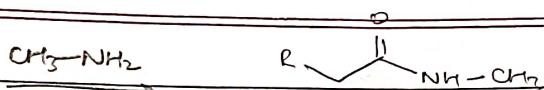
Benzyl alc. & Phenol give no CAN test

REACTANTS

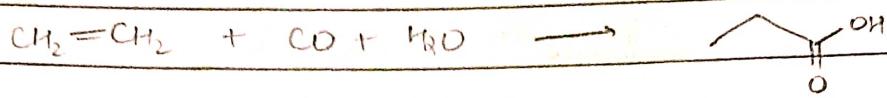


(Hell-Volhard-Zelensky reaction)

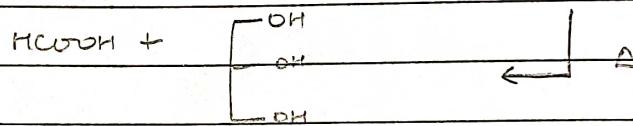
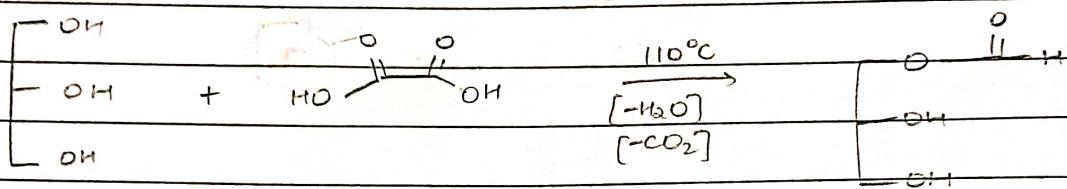




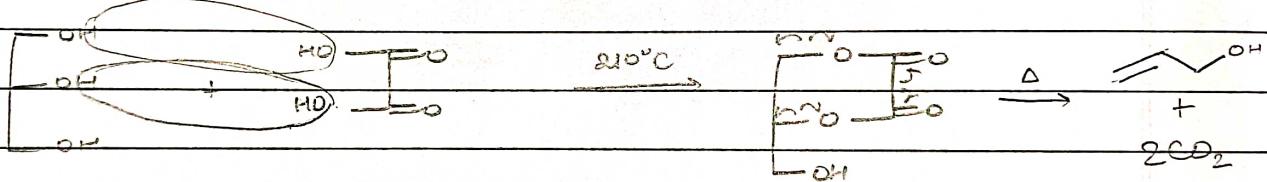
• Koch Reaⁿ



• Prepⁿ of Formic Acid

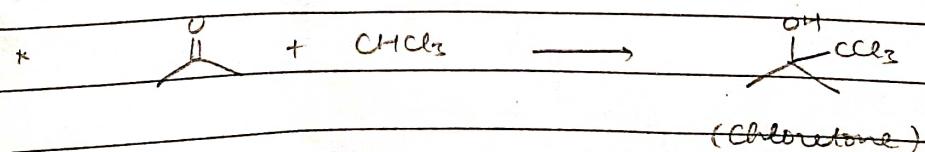
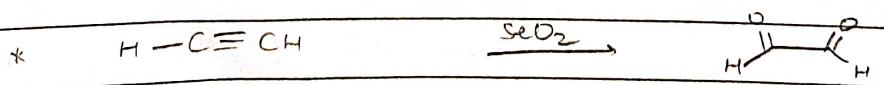
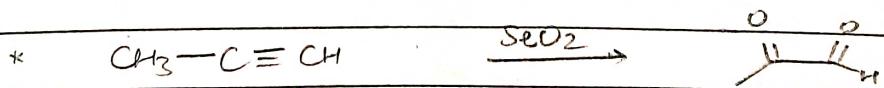


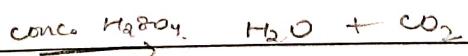
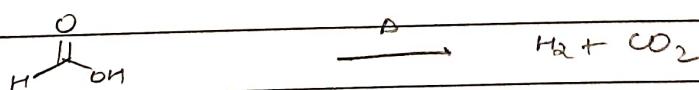
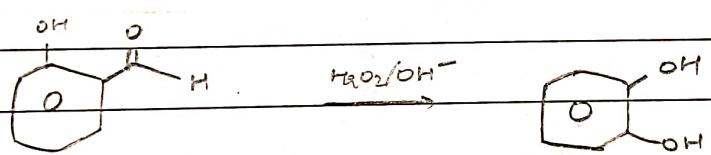
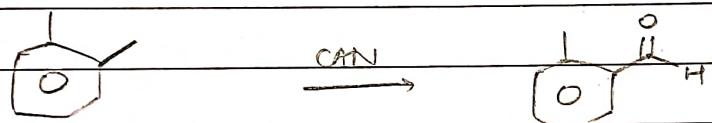
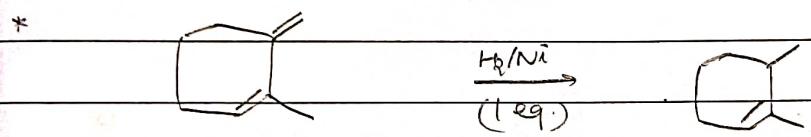
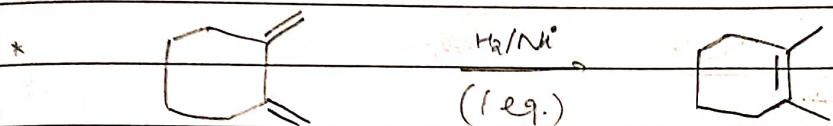
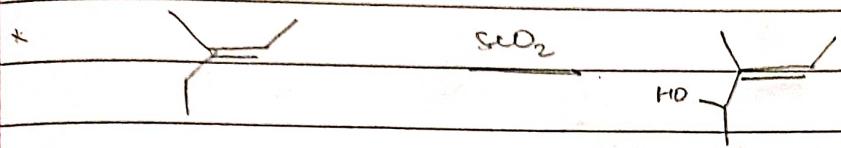
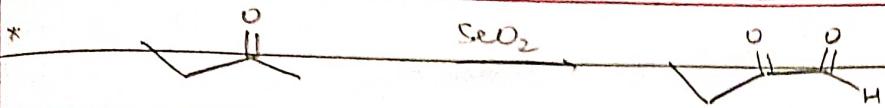
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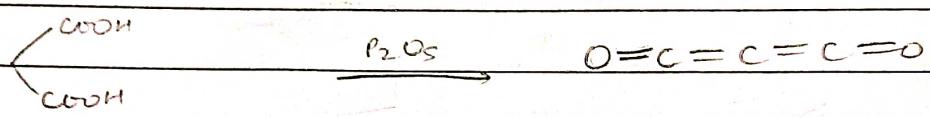
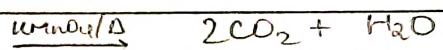
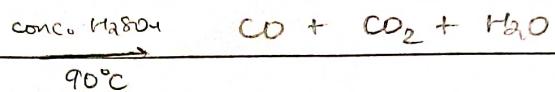
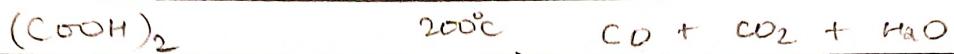


* (For AITS Only)

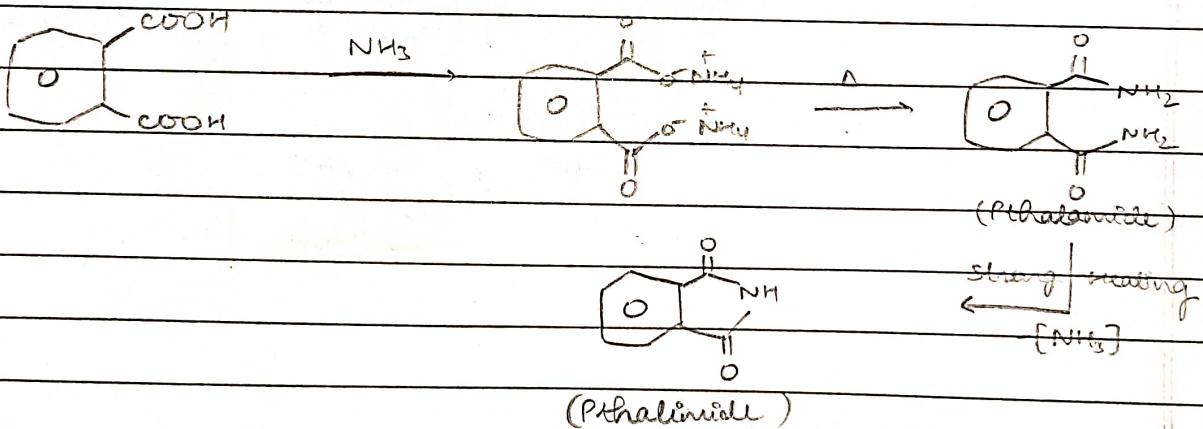
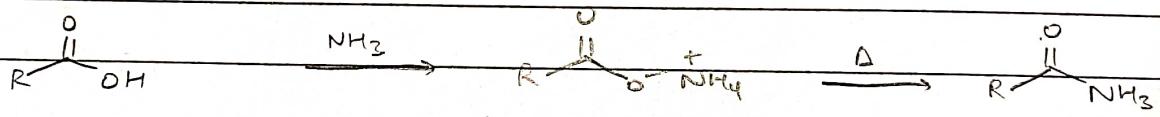
→ Misc. Reaⁿ



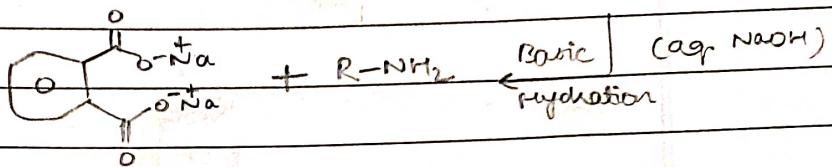
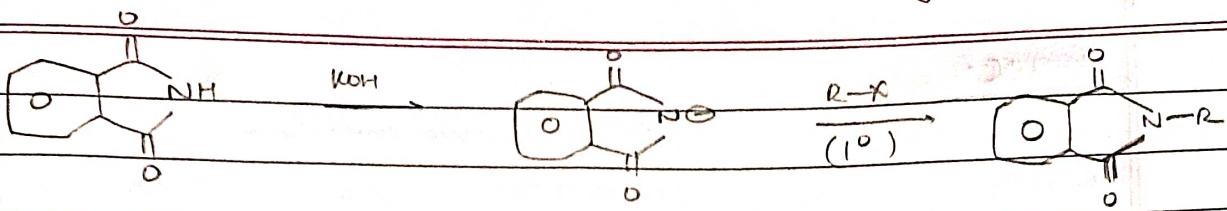




→ With NH_3

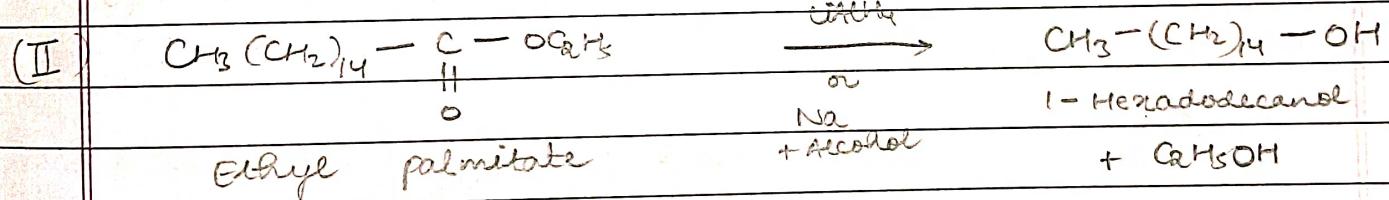
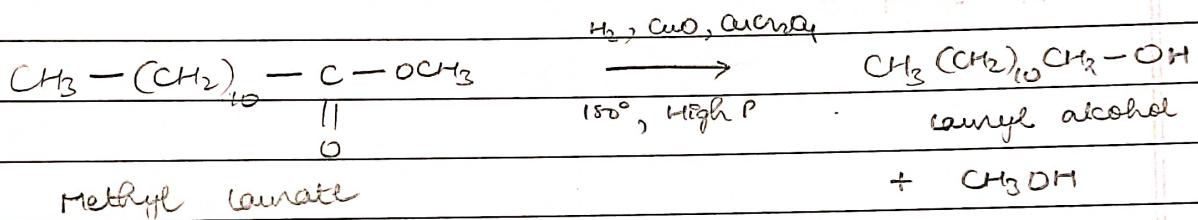


- Gabriel - Pthalimide reagent - Used to prepare aliphatic 1° amines



→ Redⁿ of Esters

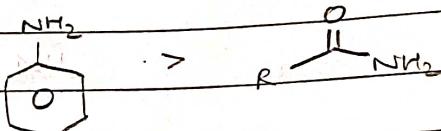
(I) Catalytic Hydrogenation



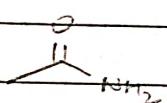
AMIDES

Amides are amphoteric in nature
& is feebly basic i.e.

B.o.S :



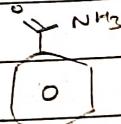
Q



(I)



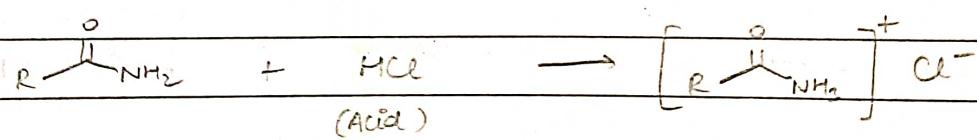
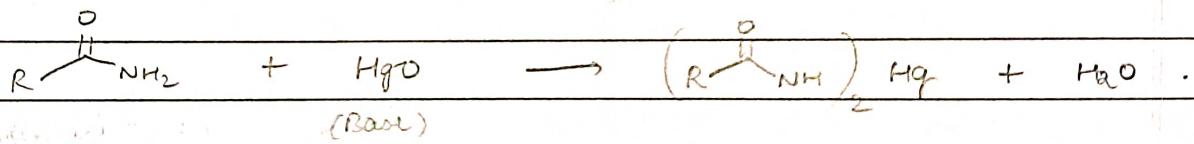
(II)

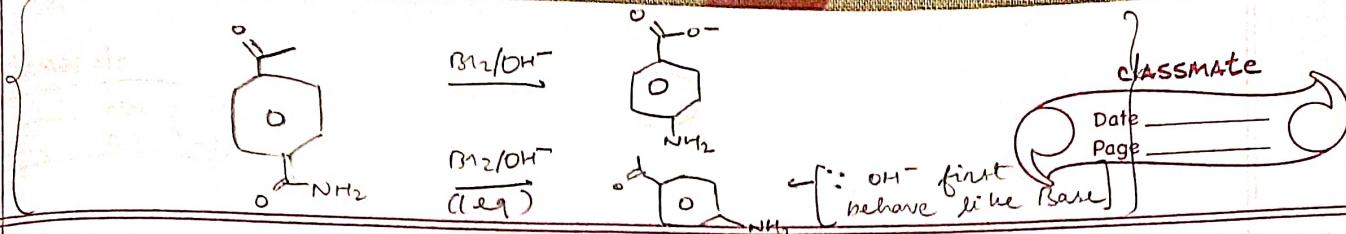


(III)

A. $(II) > (I) > (III)$

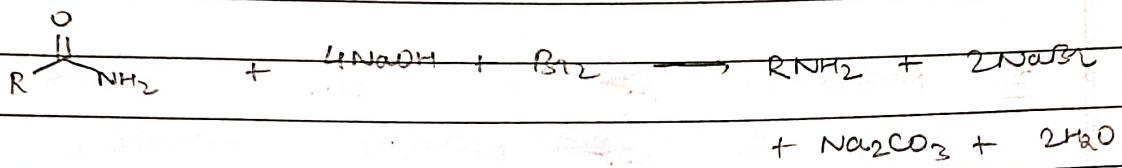
↳ (cross conj)





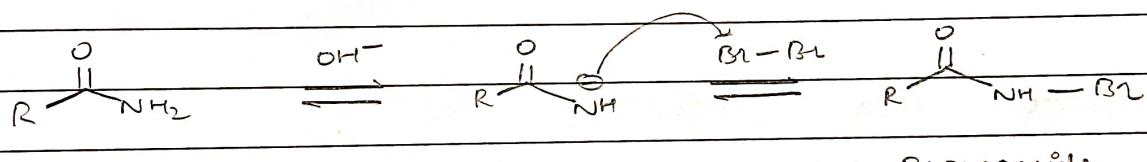
Hoffmann - Bromamide Reaⁿ

or Hoffmann - Degradation



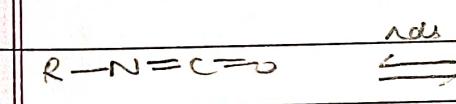
Reagents : Br_2/OH^- , Br_2/NaOH , Br_2/KOH , $\text{Br}_2/(\text{CaO})_2$, $\text{Br}_2/\text{Ba}(\text{OH})_2$
 KOBz , NaOBr
 Br_2/Base

Mechanism



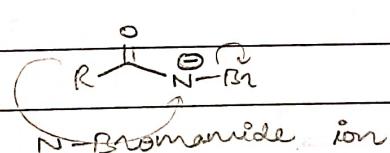
N - Bromamide

(Ist intermediate)



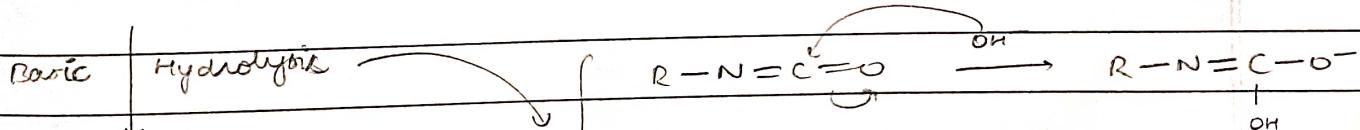
Alkyl cyanate

(IInd intermediate)



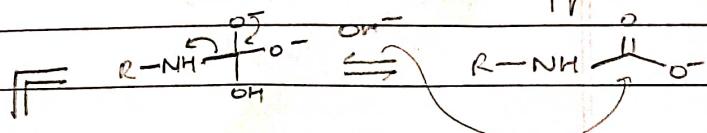
N - Bromamide ion

(IInd intermediate)



$\text{R}-\text{NH}_2 + \text{CO}_2$

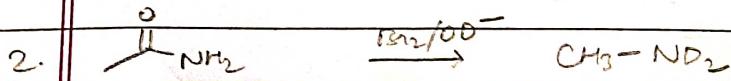
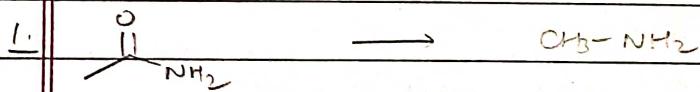
$\text{R}-\text{NH}_2 + \text{CO}_2$

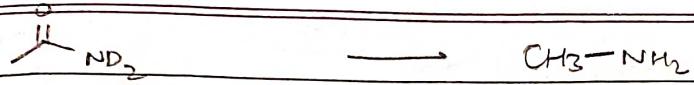
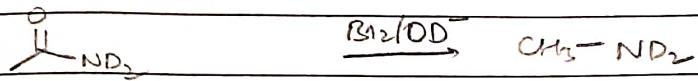
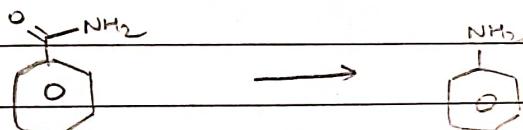
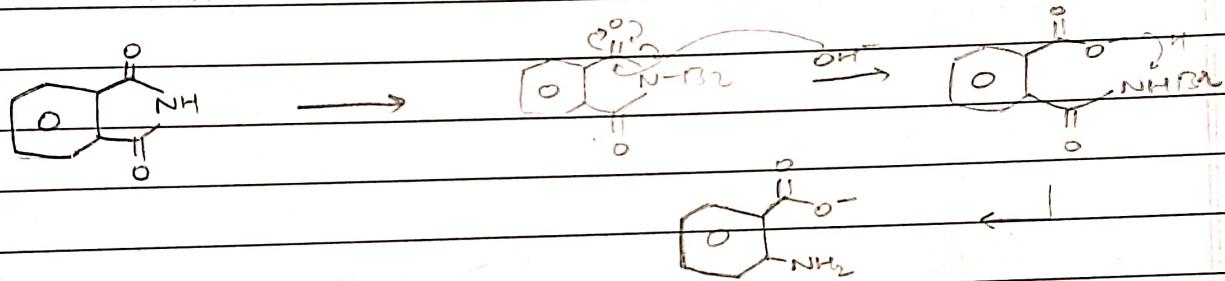
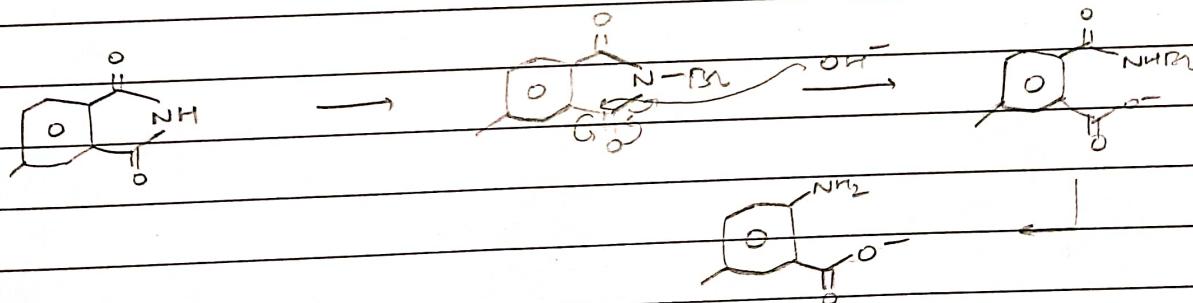
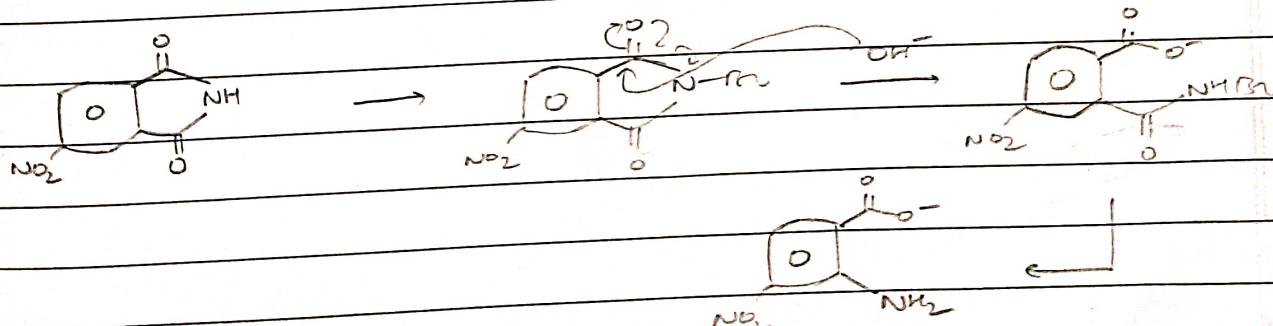


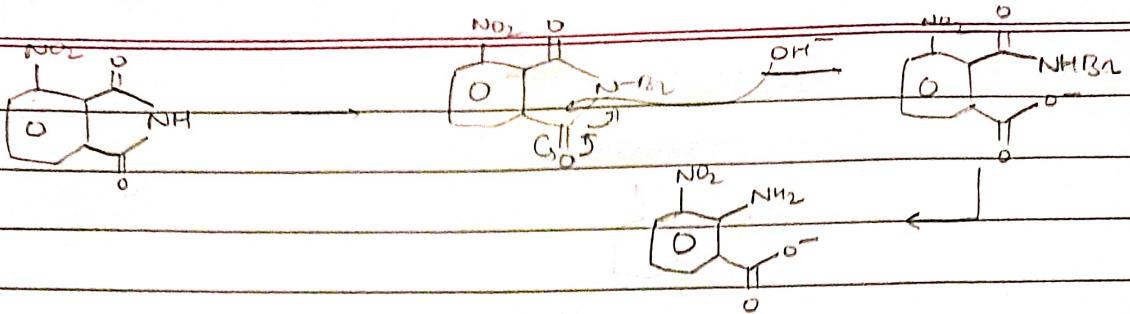
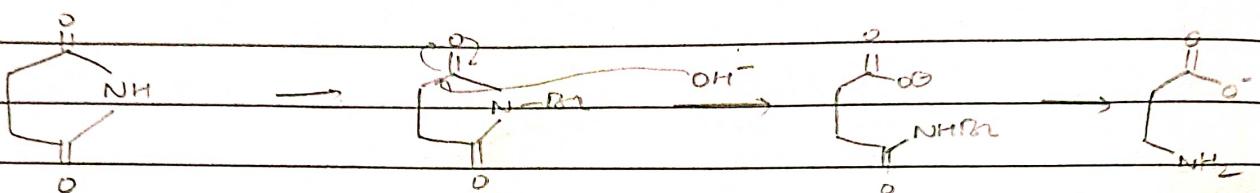
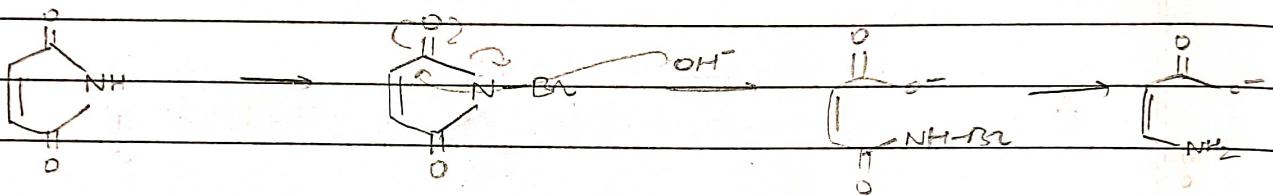
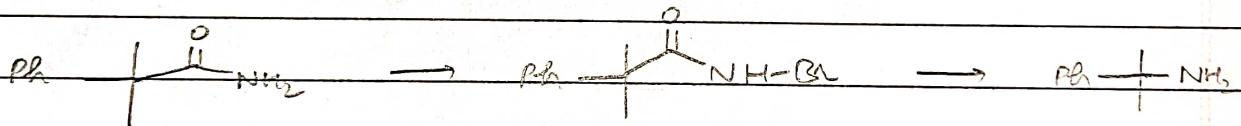
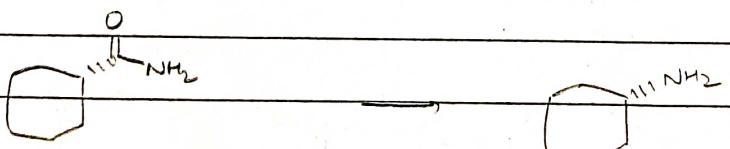
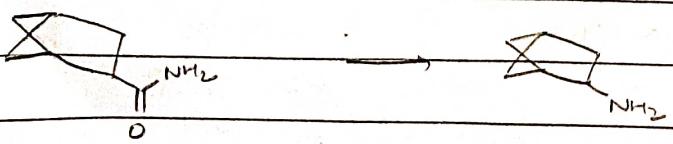
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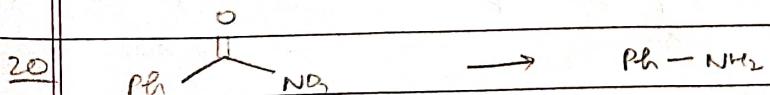
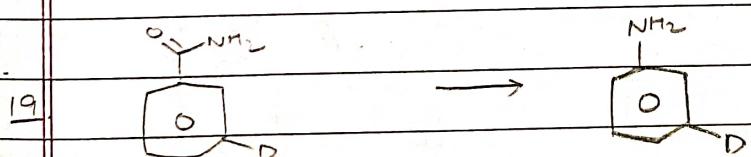
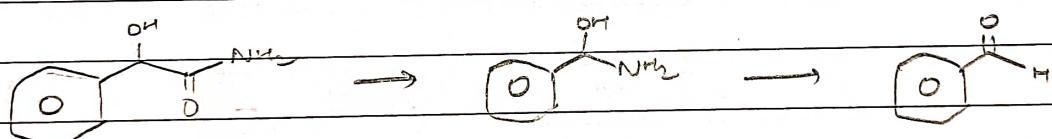
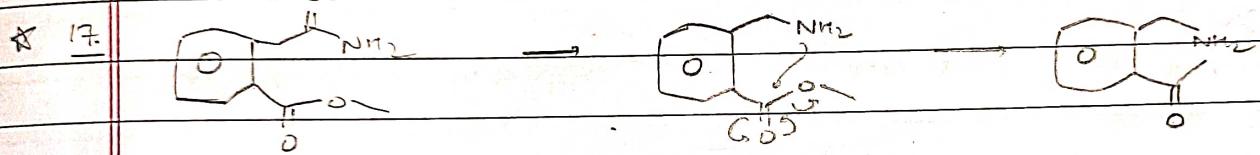
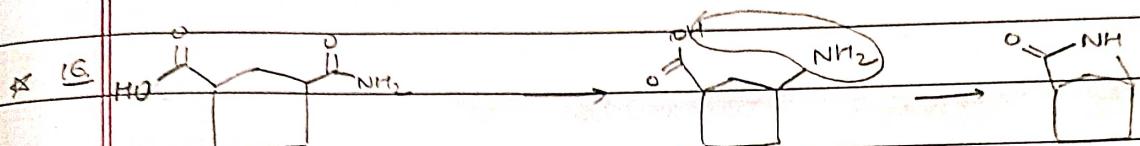
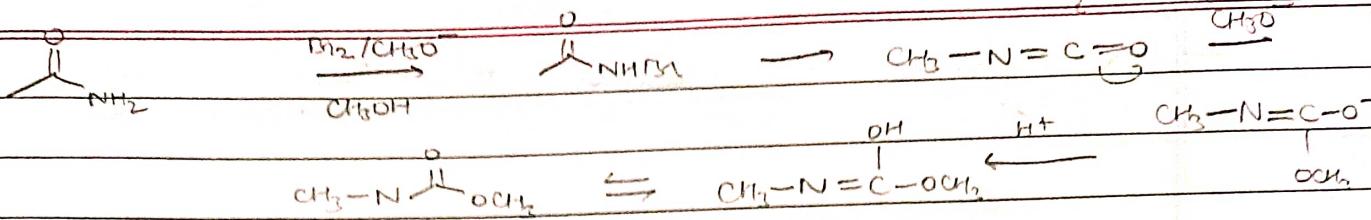
1. Reacⁿ is purely intramolecular
2. Product is ${}^1\text{o}$ amine
3. Migration of R group prevents formation of Nitrene (unstable)
 \therefore Nitrene is not an intermediate
4. Retention in migration (rule)
5. H of N in product come from medium of basic hydrolysis, not the reactant.

Q Write the product

(Medium R_2/OH^- unless specified)

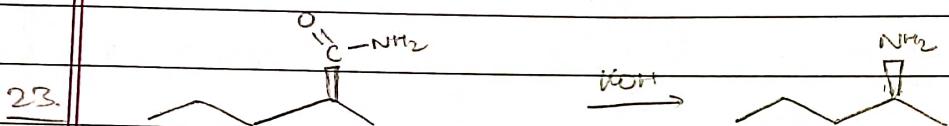
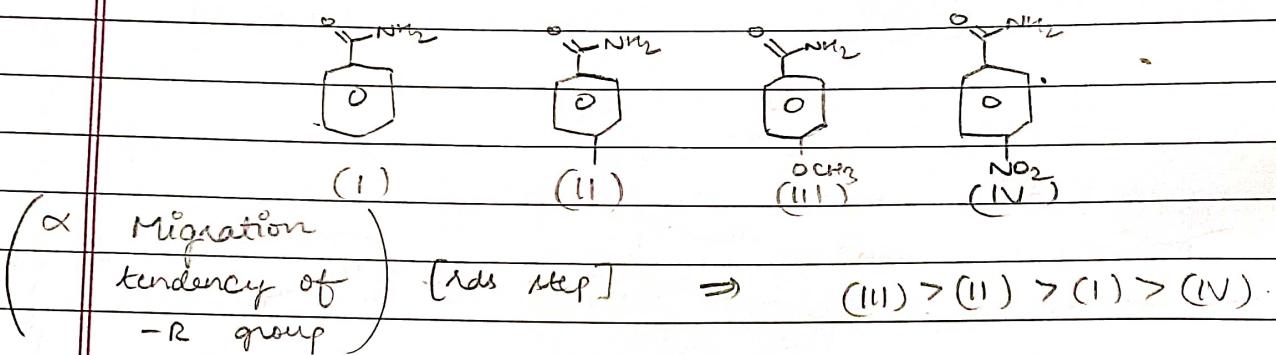
3.4.5.6.7.8.

9.10.11.12.13.14.

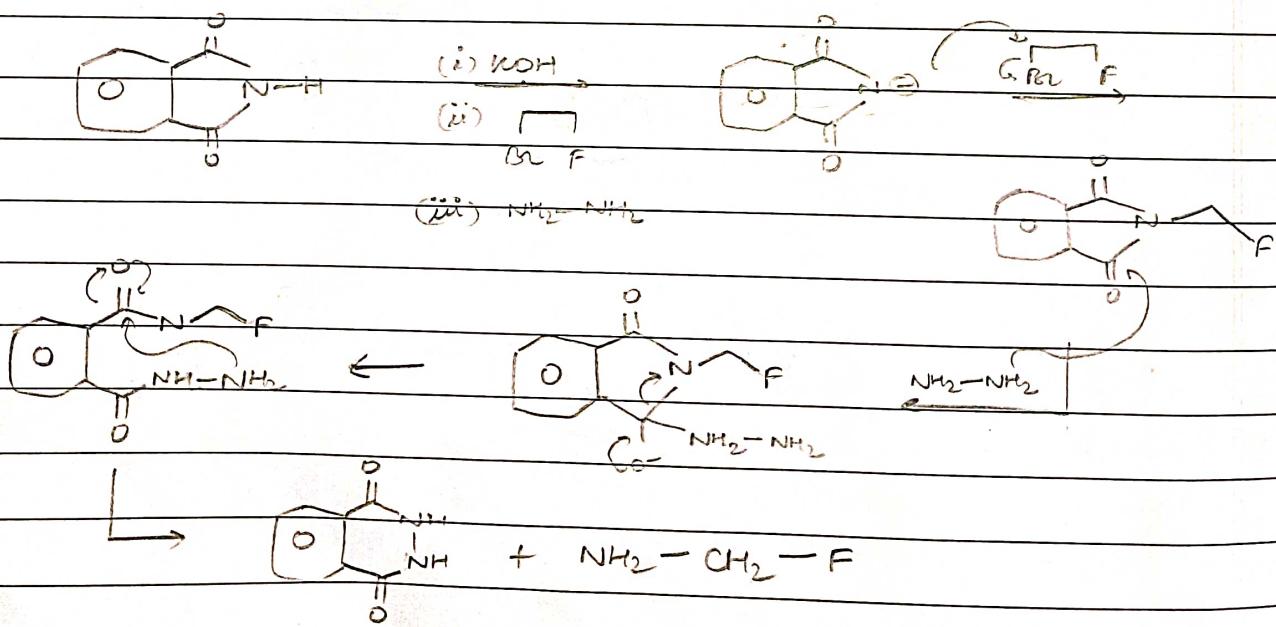




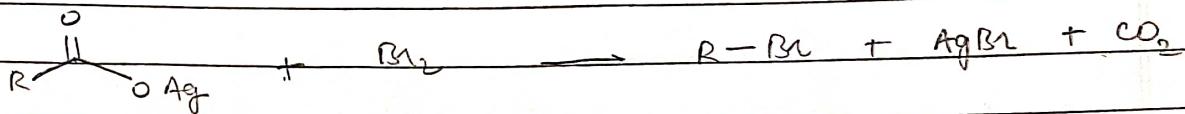
* 22. Rate of Hoffmann Bromamide Reacⁿ



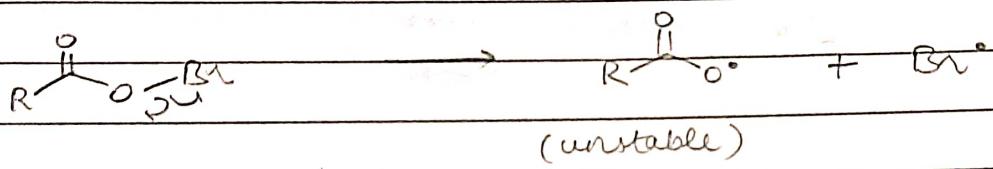
* 24.



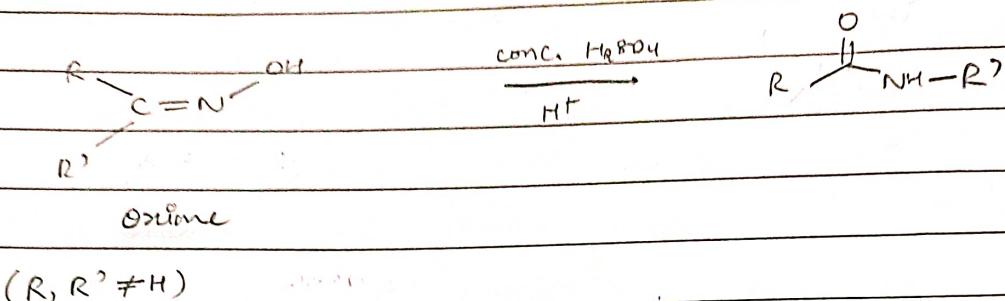
Hundidicker non - (Only in case of Br)



Mechanism

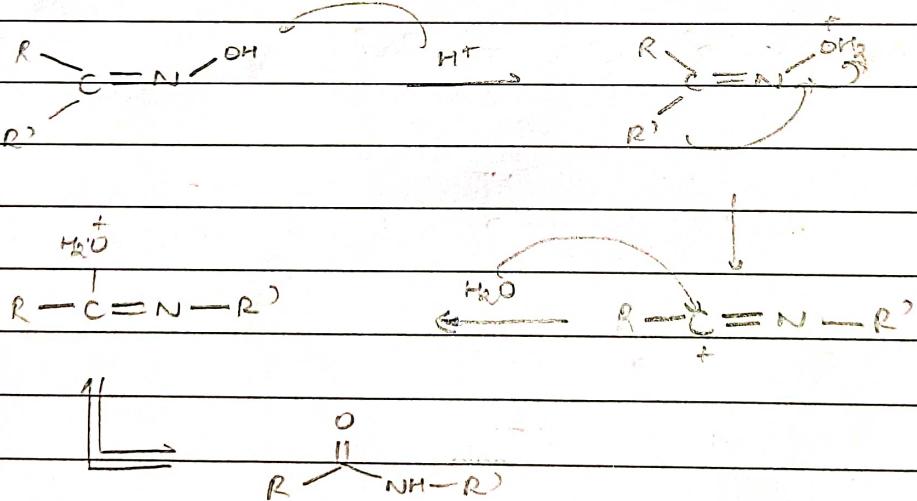


• Beckmann Rearrangement -

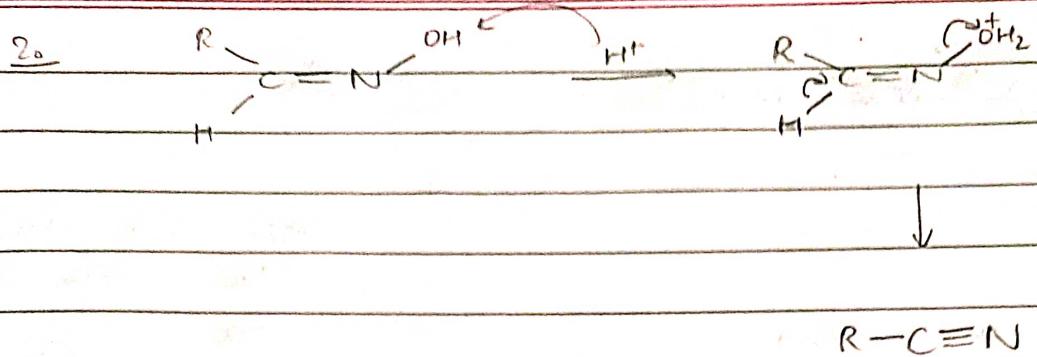


Reagents : H^+ , PCl_5 , P_2O_5 , P_2O_{10} , SO_3 , POCl_3 ,
 H_2SO_4 , AlCl_3 , SO_2Cl_2

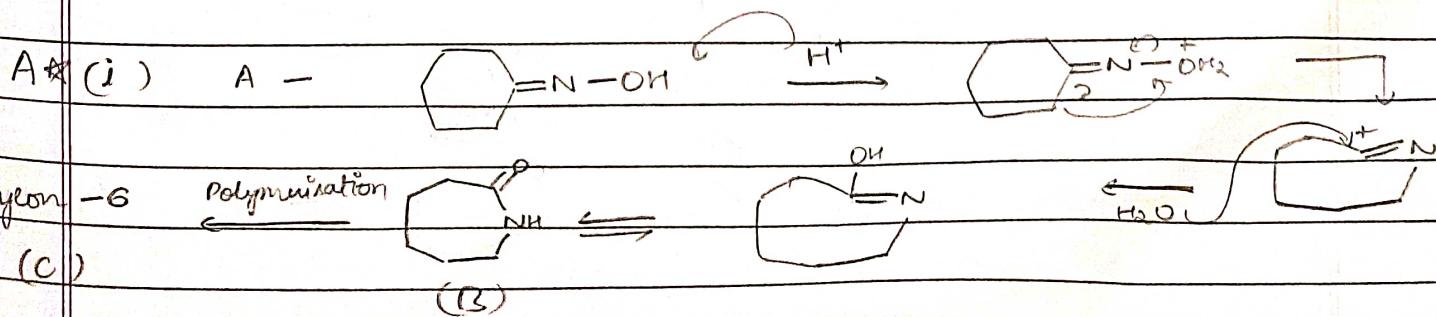
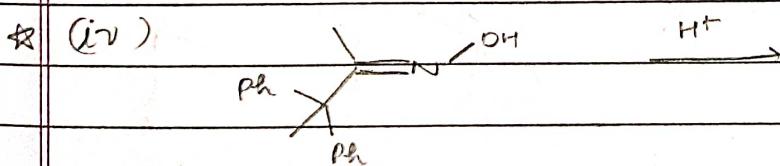
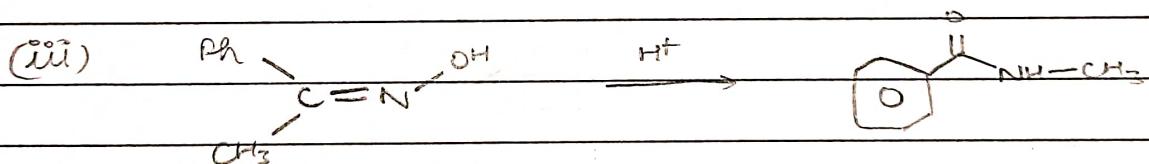
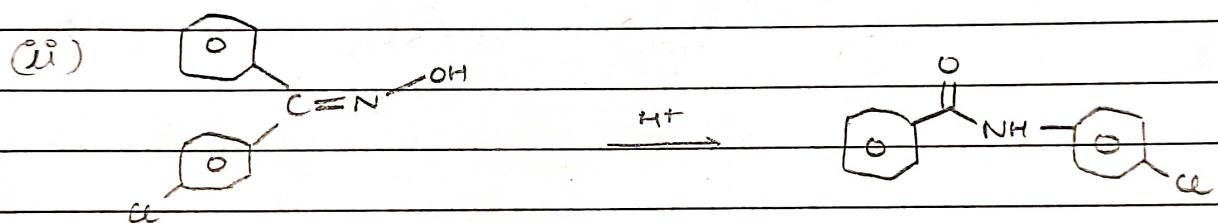
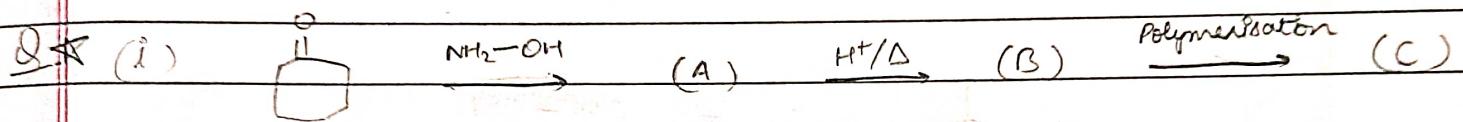
Mechanism



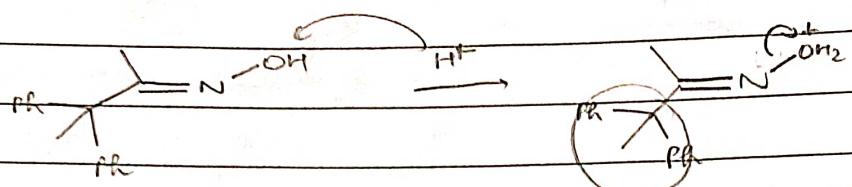
NOTE: 1. Alkyne group anti to -OH migrates.
 No significance of migration tendency.



Q. 3. Retention of migrating group



★ (iv)

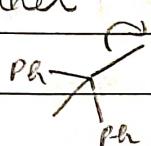


this bond should have been broken

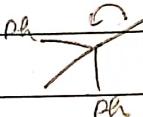
But, due to

it being extremely
bulky, it rather

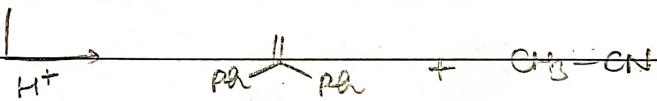
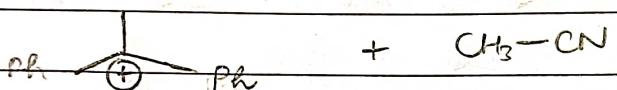
break like



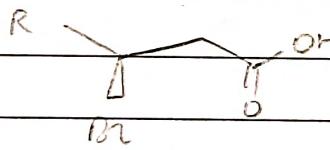
like



So,



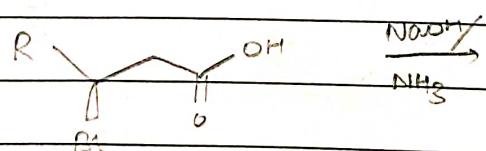
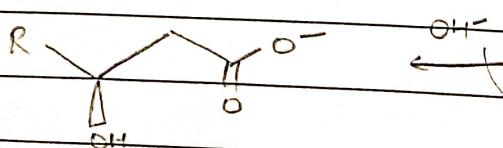
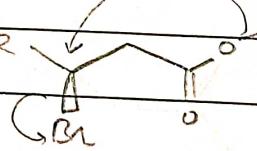
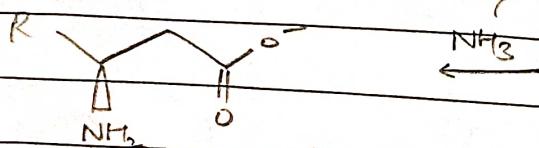
★ Q.



NaOH

NH3

A.

NaO⁺
NH₃OH⁻NH₃

FORMIC ACID

