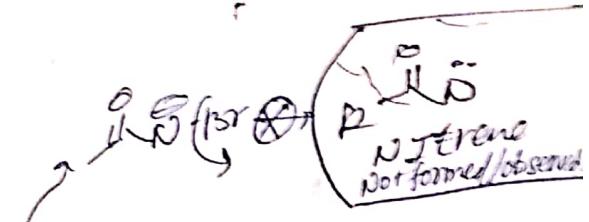
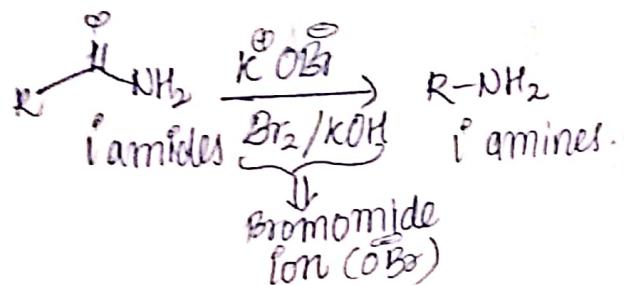
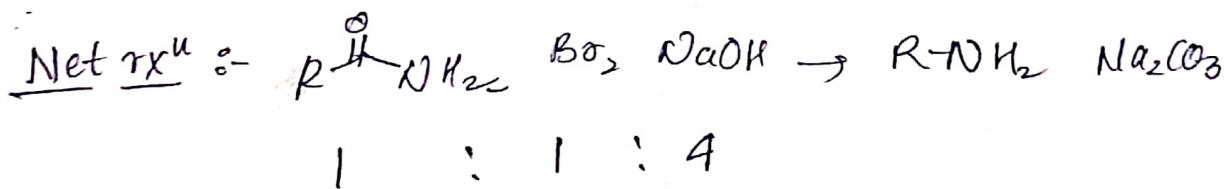
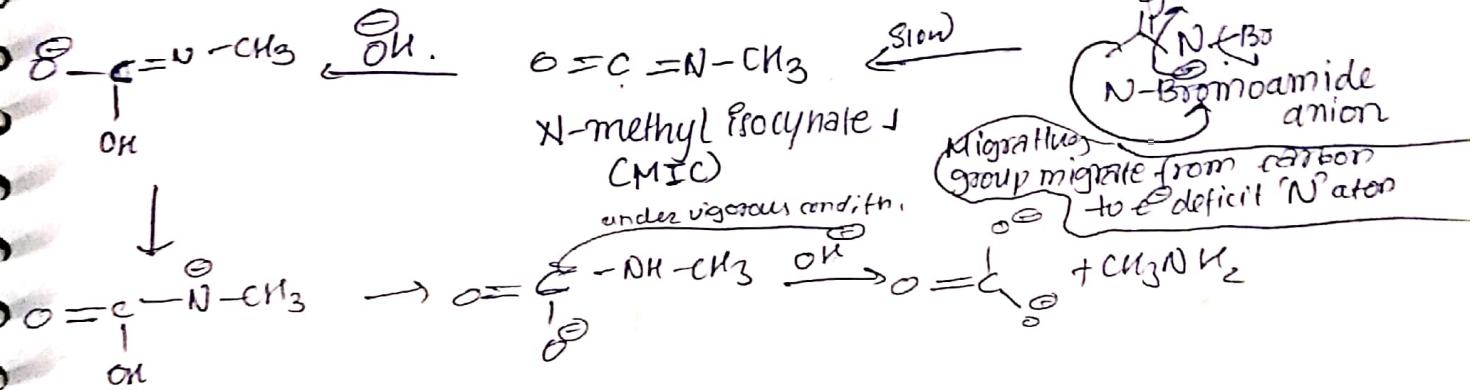
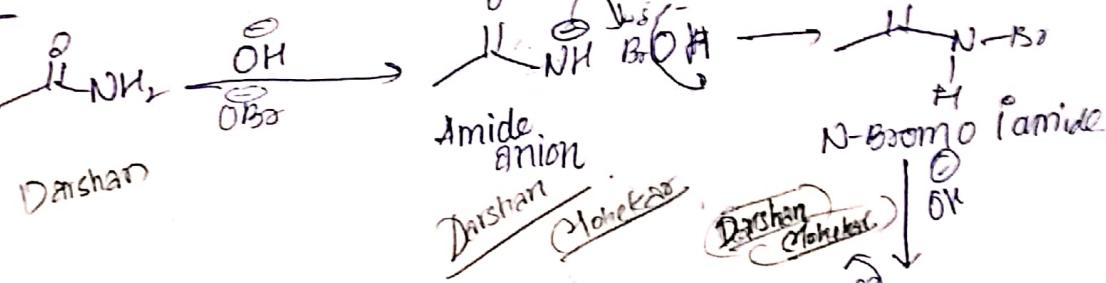


Carboxylic Acids and its Derivatives

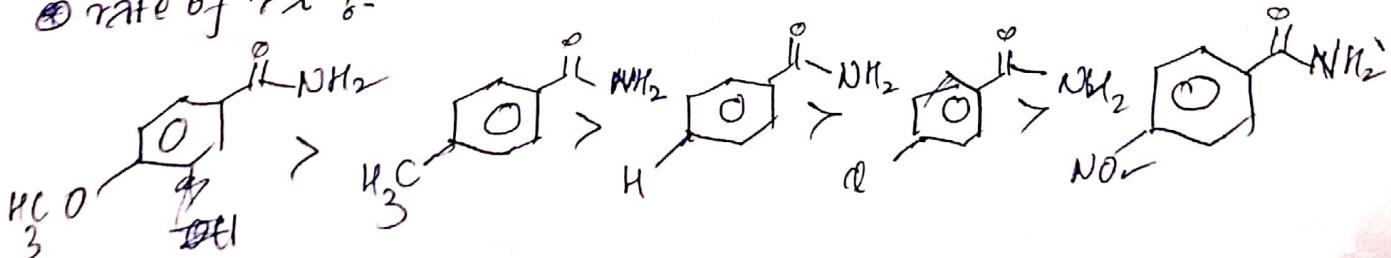
A Hoffman Bromamide rxn / degradation



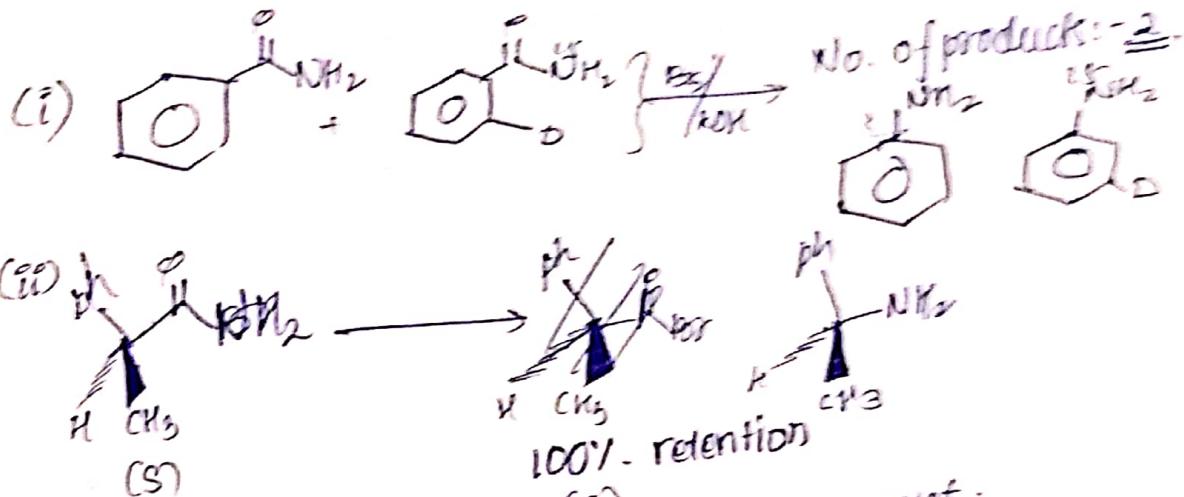
Mechanism



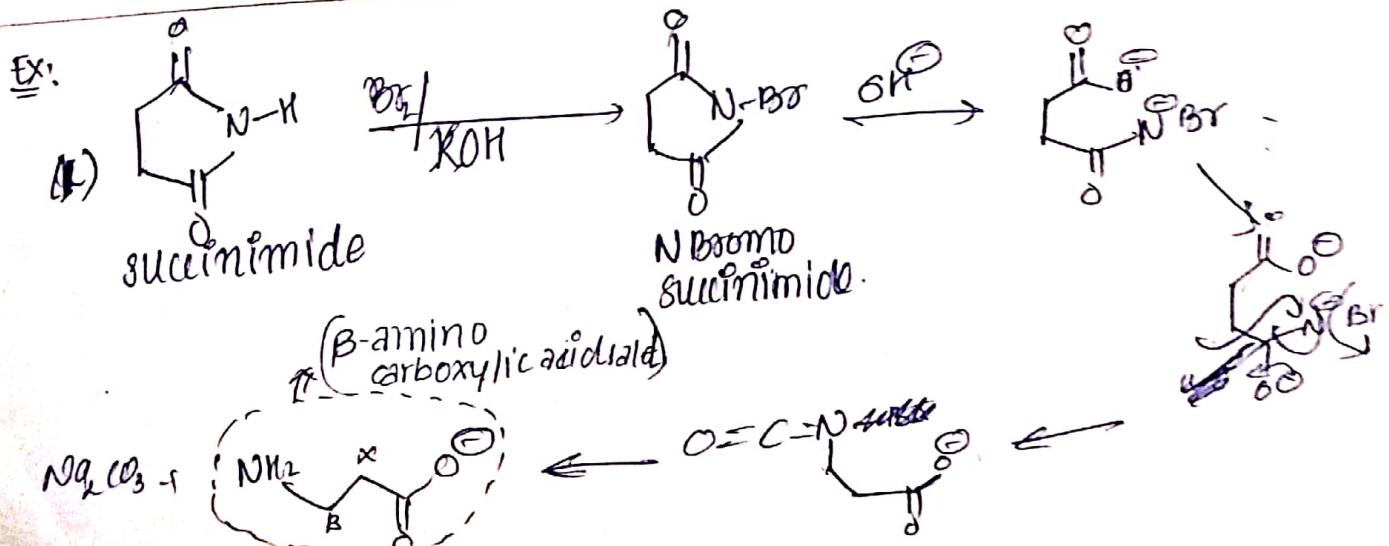
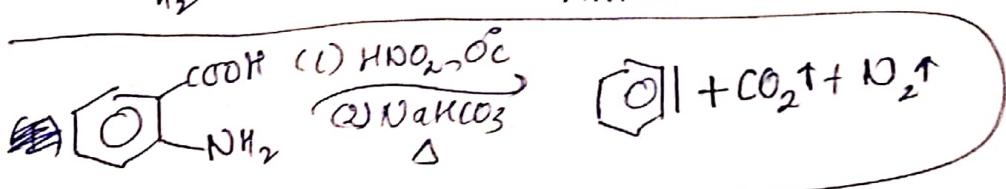
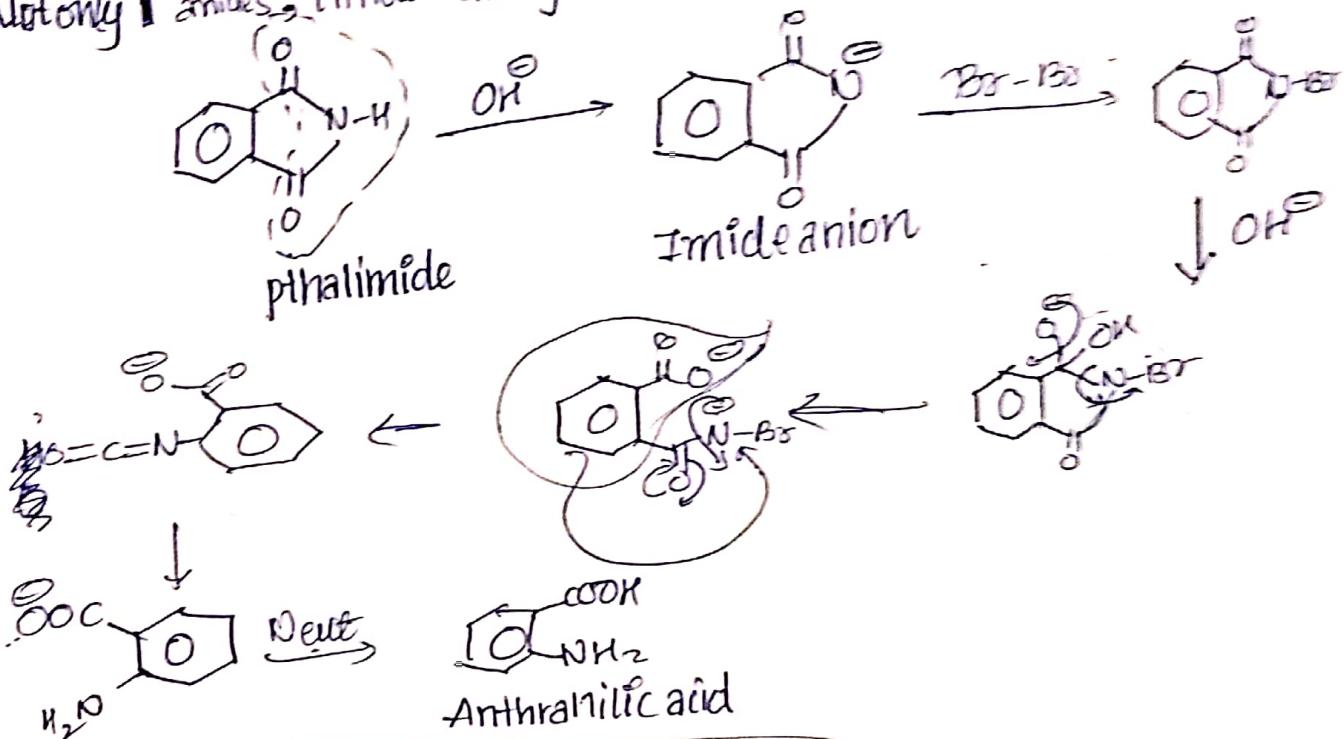
- ⊕ 2°-amides doesn't give this rxnⁿ
- ⊕ 3°-amides doesn't give this rxnⁿ.
- ⊕ rate of rxnⁿ-



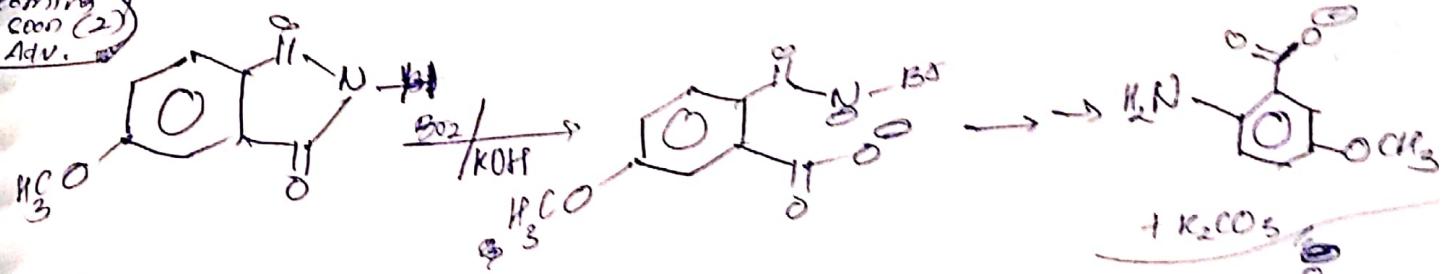
④ Intramolecular rearrangement.



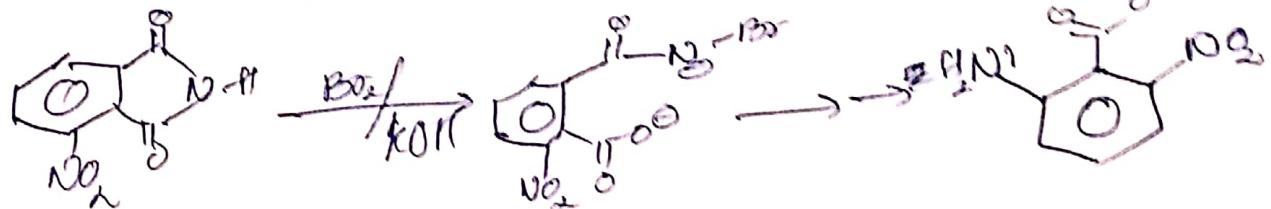
⑤ Not only amides, imides also give this rearrangement.



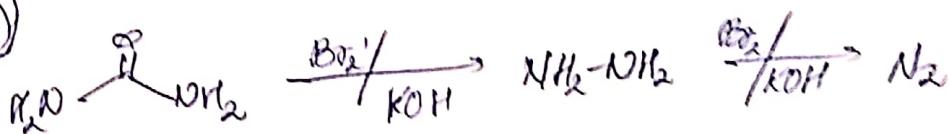
coming soon (2)
Adv.



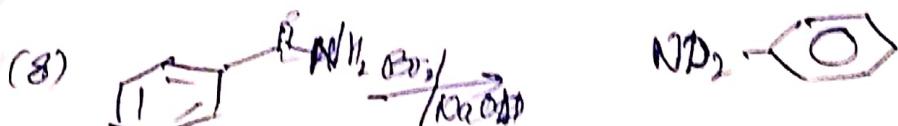
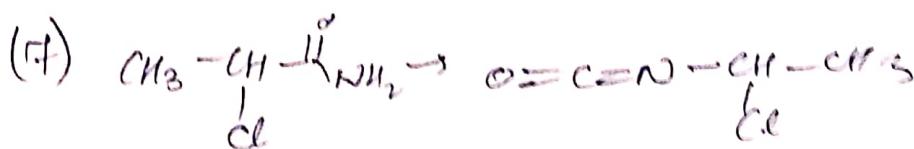
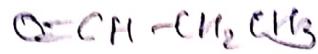
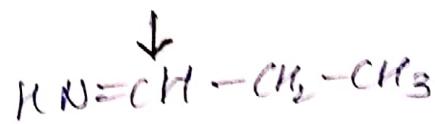
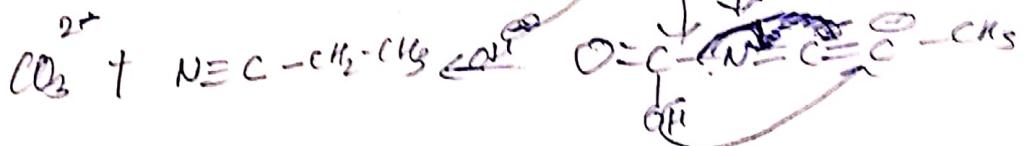
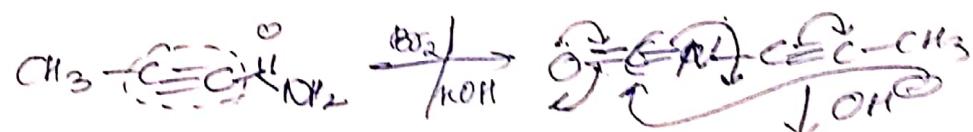
(2)



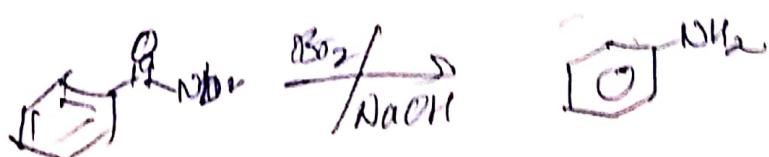
coming soon (4)



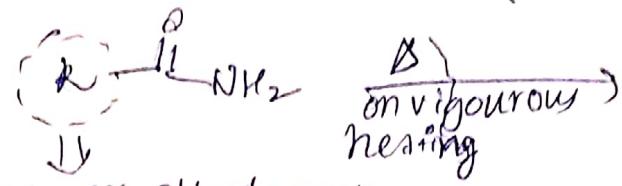
(5)



(9)



NOTE

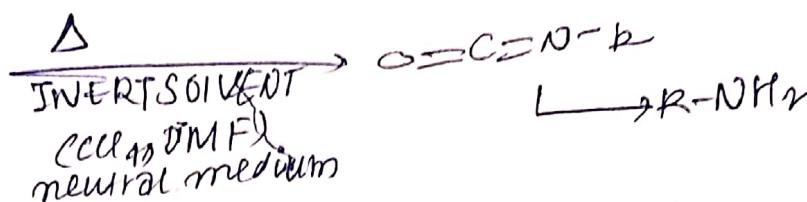
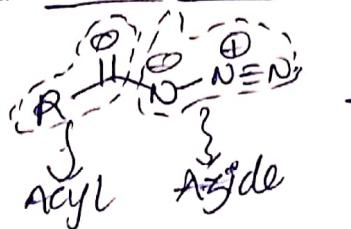


linear alkyl group

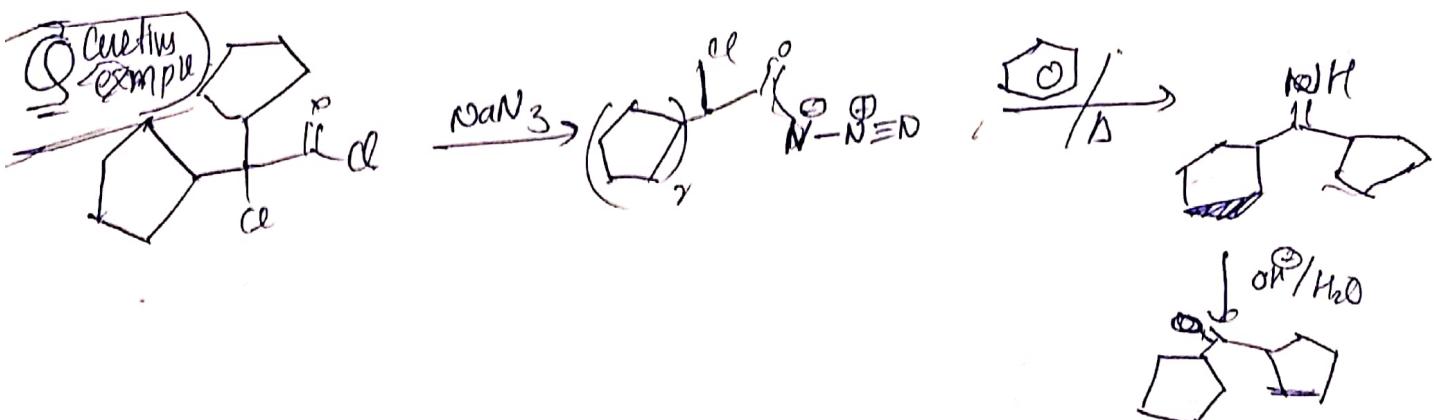
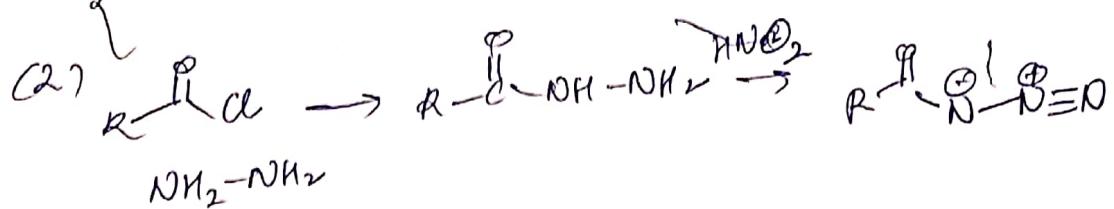
with 7 or more than
7 carbon doesn't get
rearrangement.



Curtius Rearrangement

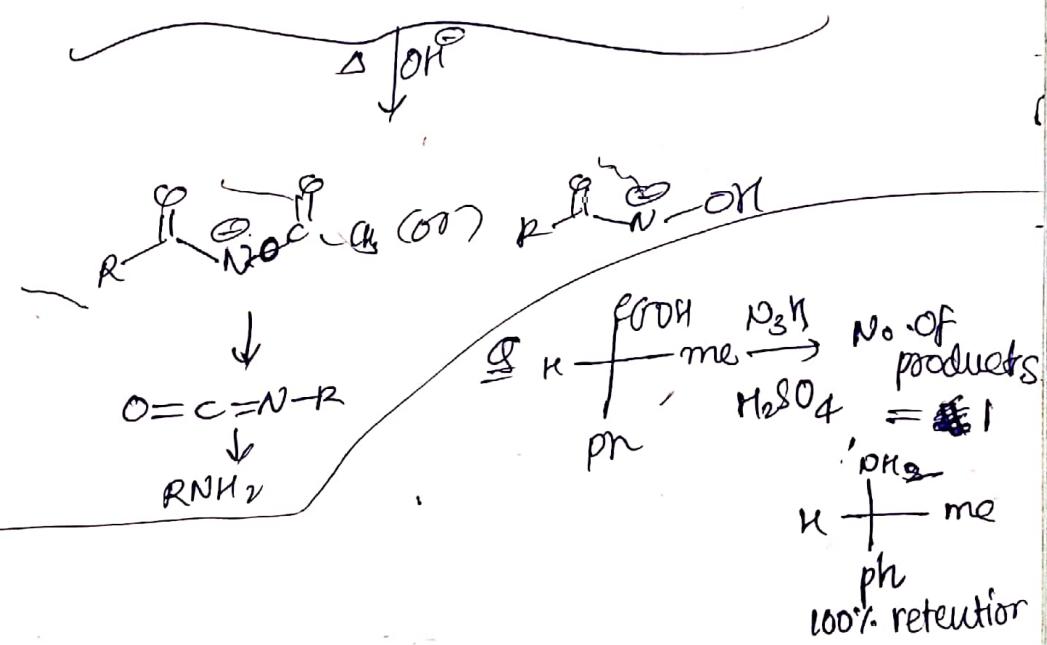
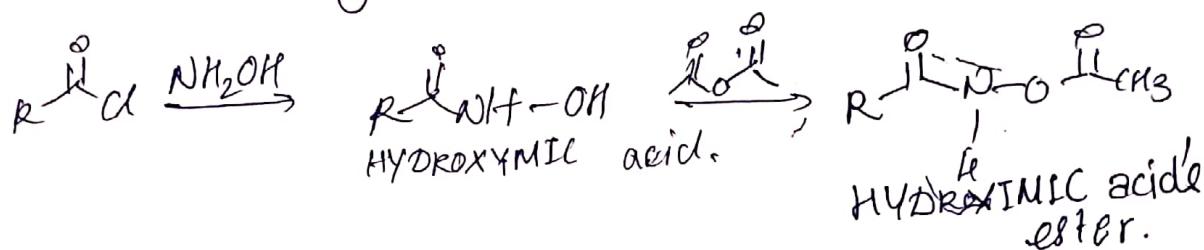


Preparation of Acyl Azide



3

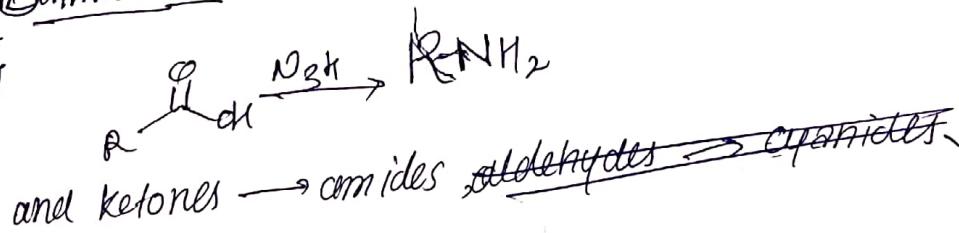
Lossen rearrangement



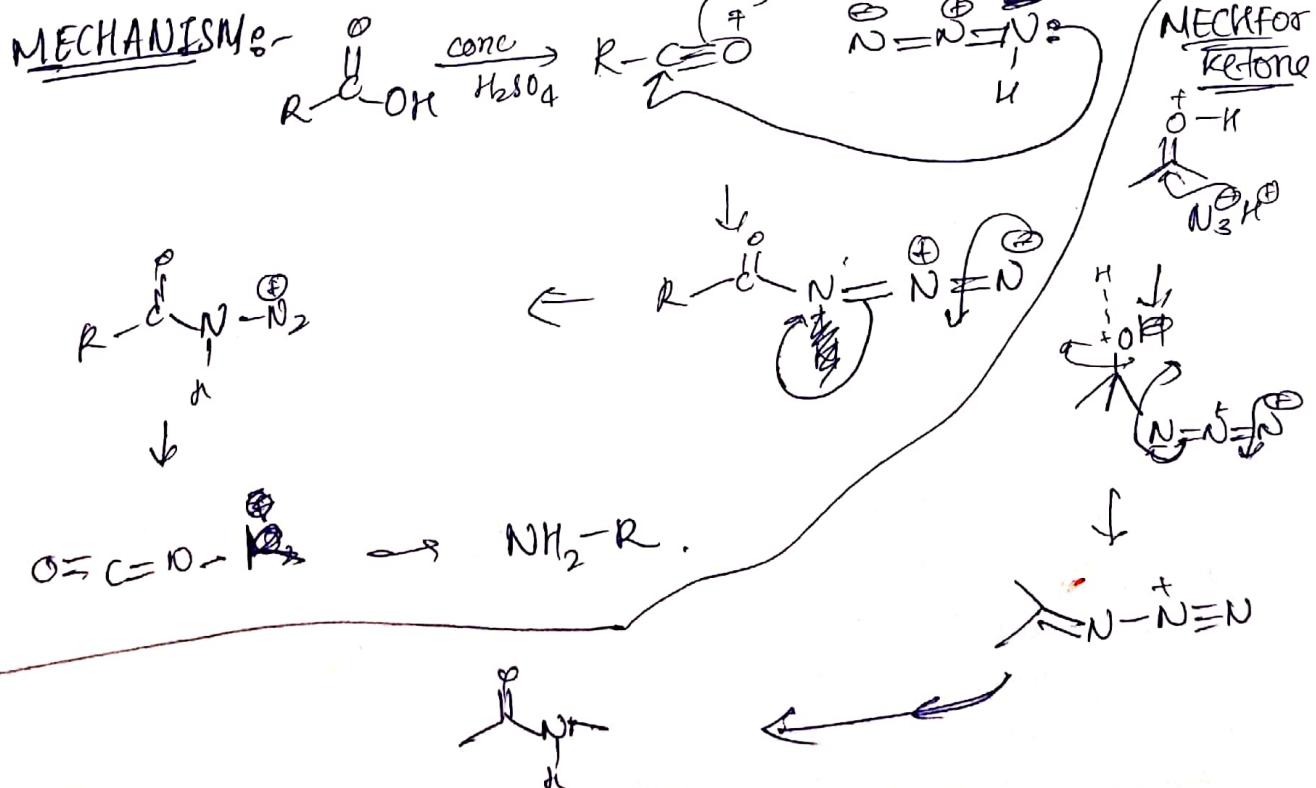
4

Schmidt Rearrangement

Imp. for
BITSAT



For Ketones, the reaction is Lossen Rearrangement



A simple line drawing of a house with a triangular roof and a vertical chimney on the right side.

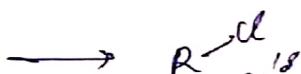
Andt-Eistet

-Ester
A carboxylic acid $\xrightarrow{\begin{array}{l} \text{(1) } \text{SOCl}_2 \\ \text{(2) } \text{CH}_3\text{N}_2 \\ \text{(3) moist } \text{Ag}_2\text{O}/\Delta \end{array}}$ next higher Homolog carbonyl acid.



$$R-\overset{\text{O}}{\underset{\text{C}}{\text{H}_2}}-\text{COOH}$$

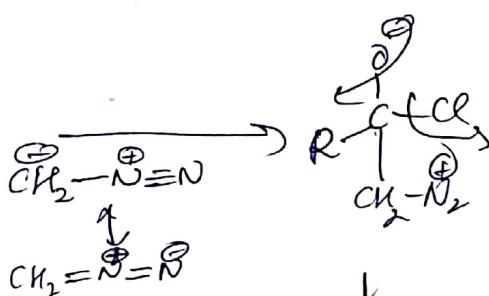
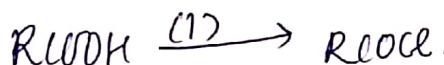
HEAD R-OK



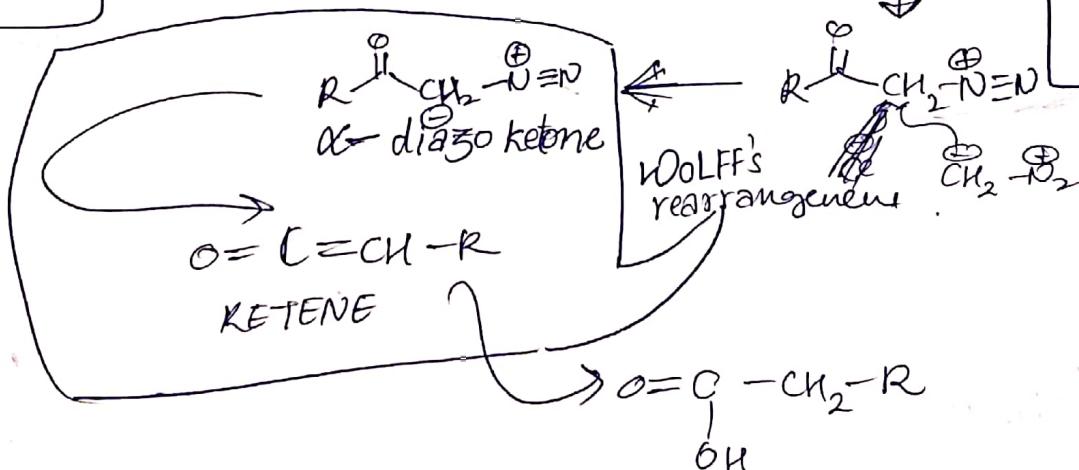
$$R\overset{9}{\text{H}}\overset{18}{\text{OH}} \rightarrow R\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}} \text{ and } R\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}} \text{ equally formed.}$$



MECH



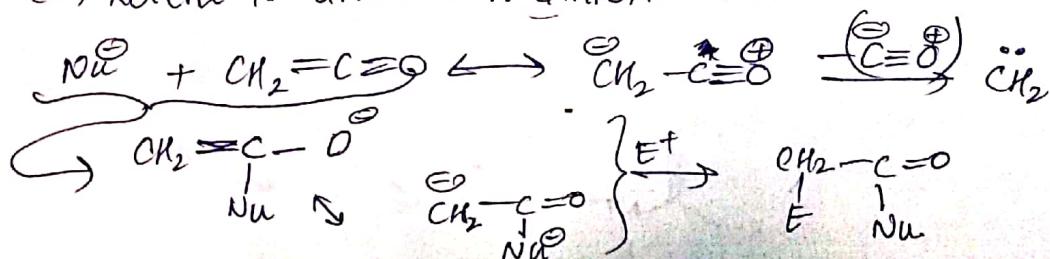
$$\text{CH}_2\text{N}_2 \rightarrow \underbrace{\text{ROH}}_{\substack{\text{acth} \\ \text{site}}} \text{ Nucleophile with others.}$$

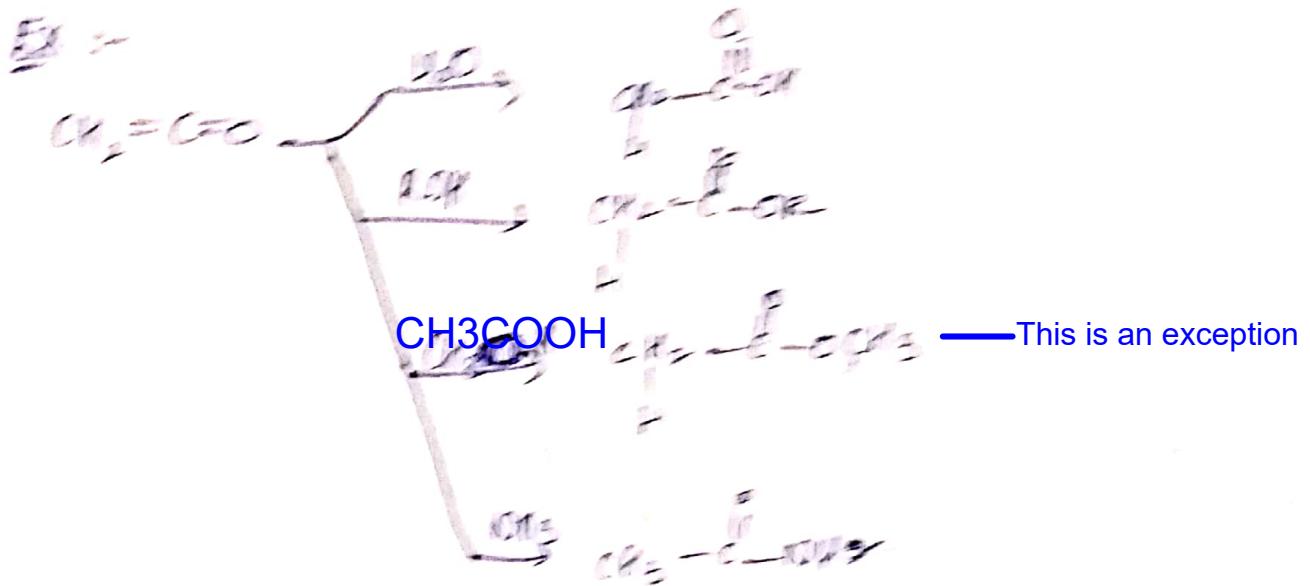


PREPARATION AND PROPERTIES OF KETENE

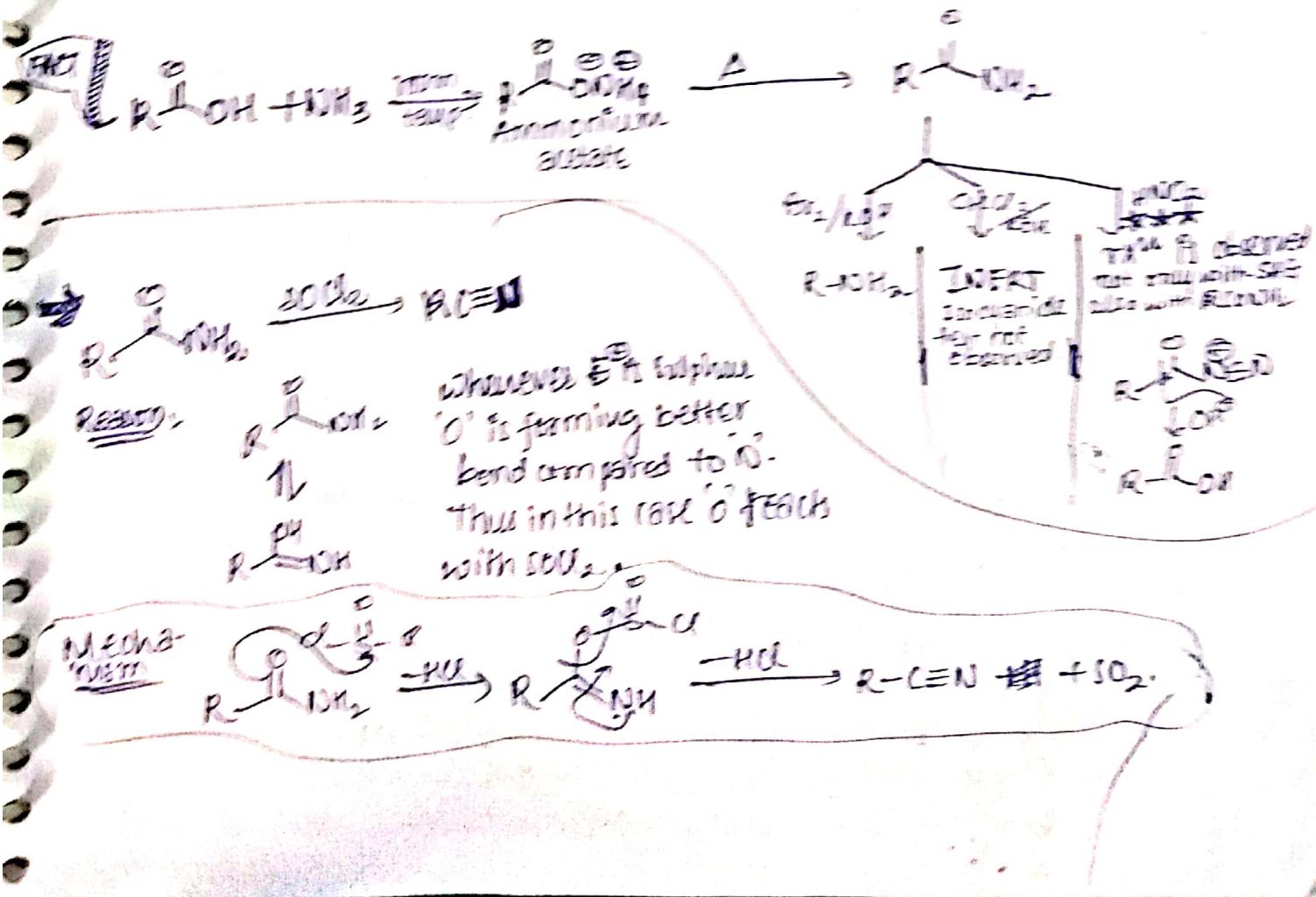


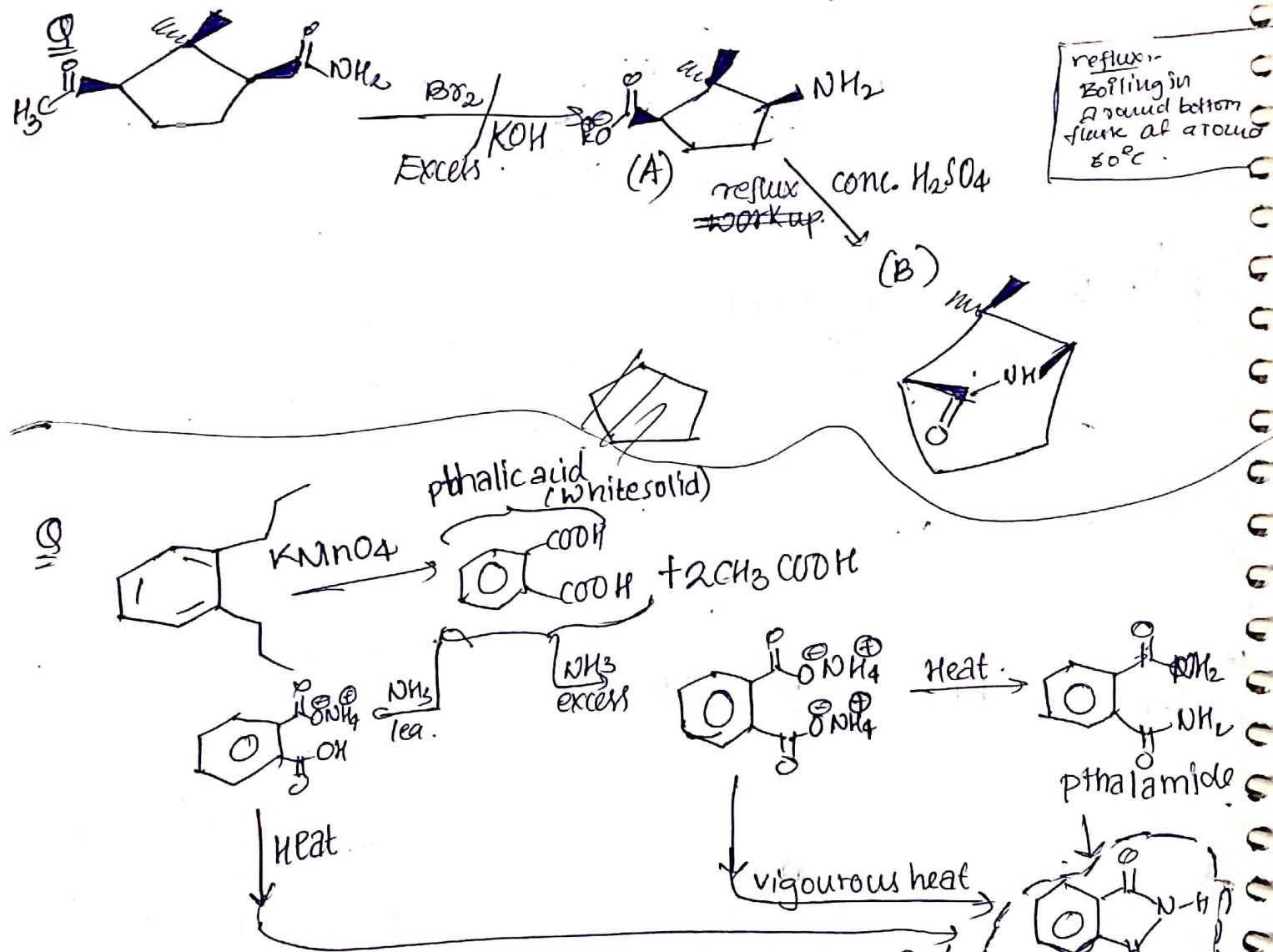
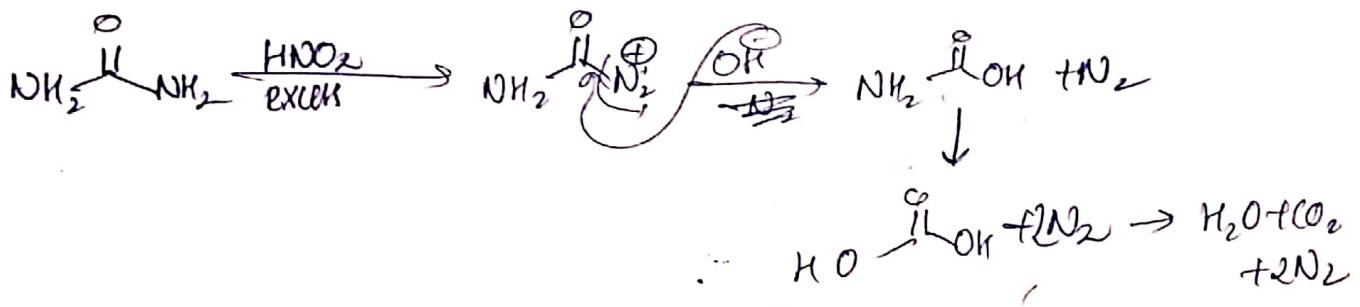
(9) Ketene is unstable it exhibits resonance.



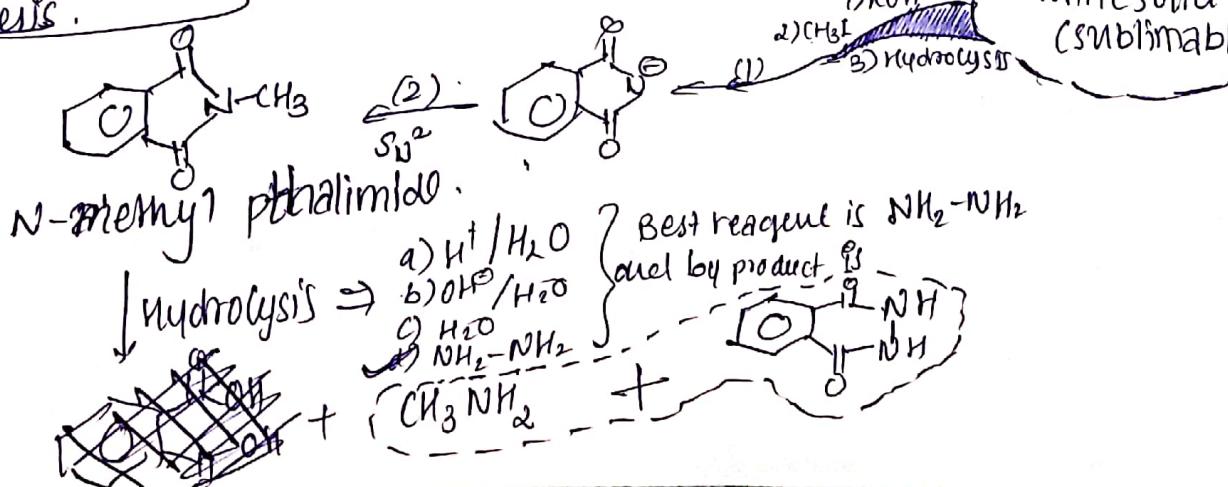


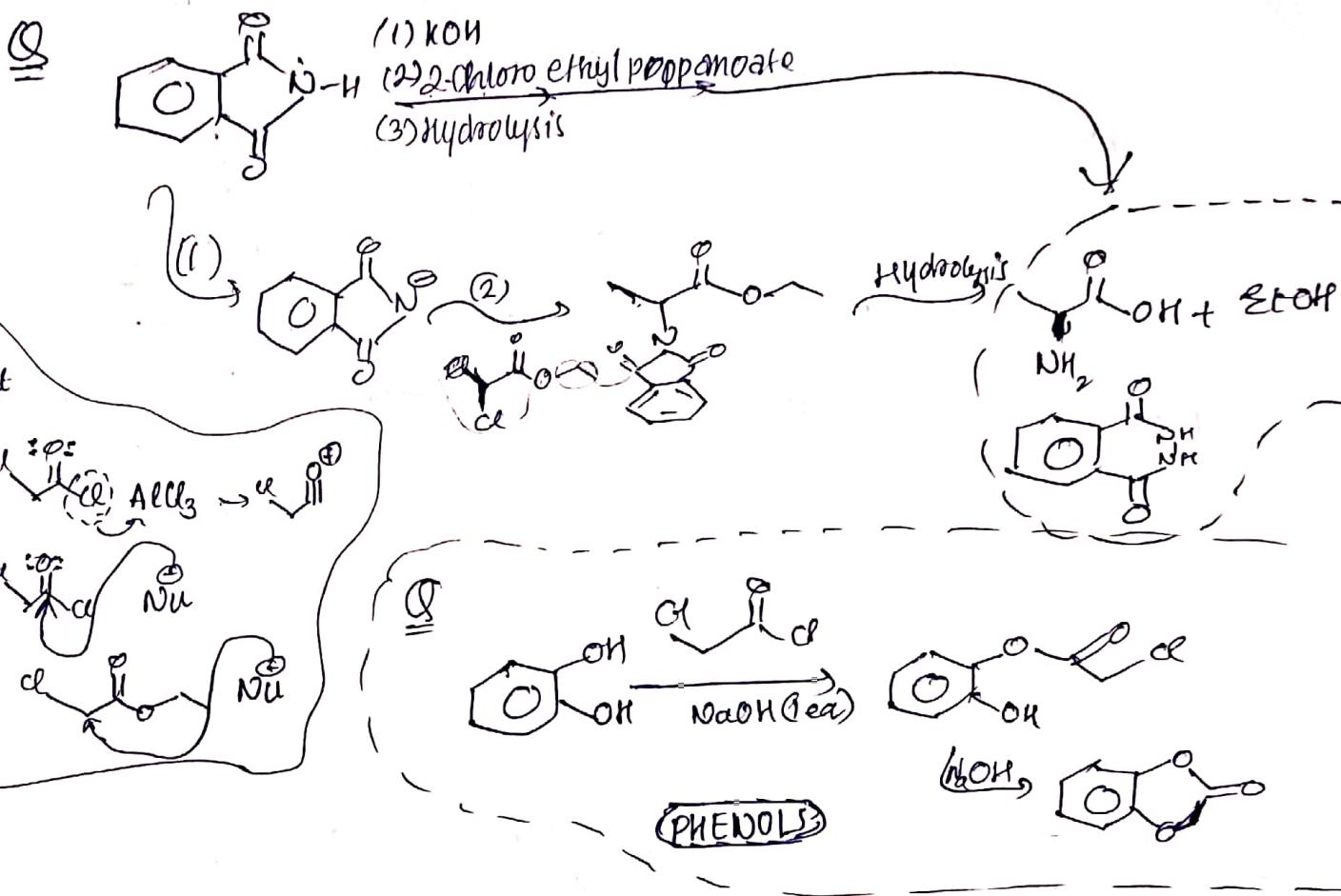
Wohl rearrangement





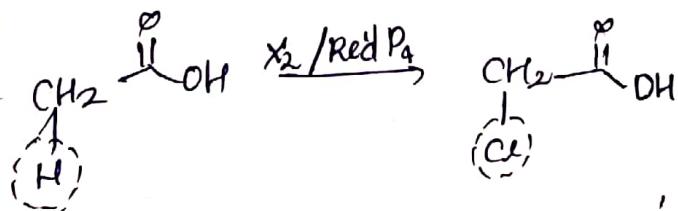
Gabriel phthalimide synthesis



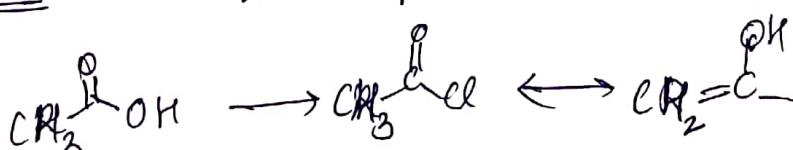


Hell-Volhard-Zelinsky rxn (H-V-Z rxn)

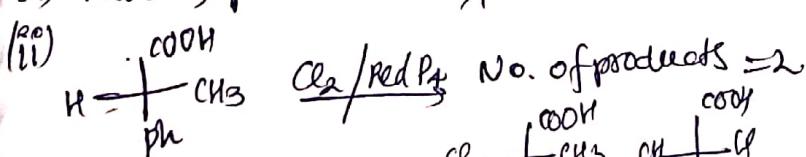
⇒ Carboxylic acids are converted to α -halo acids by means of



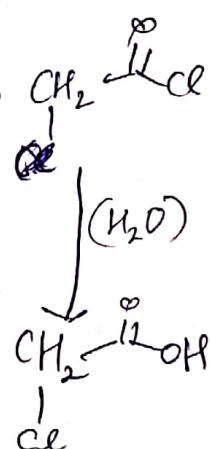
MECHANISM : $\text{X}_2 + \text{Red P}_4 \rightarrow \text{PX}_3 \xrightarrow{\text{O}_2} \text{PX}_5$

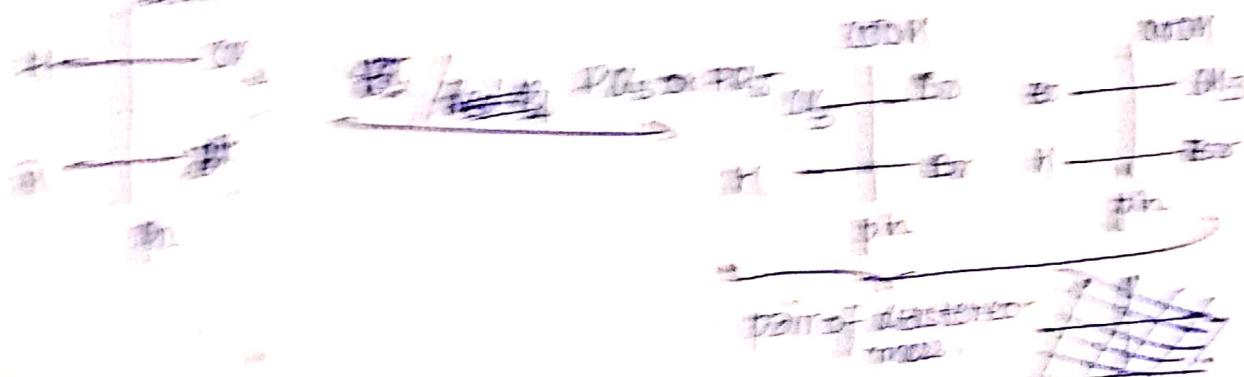


(i) HCOOH , phenol, $\text{C}_6\text{H}_5\text{OH}$, etc, don't give this rxn.



pair of enantiomers.

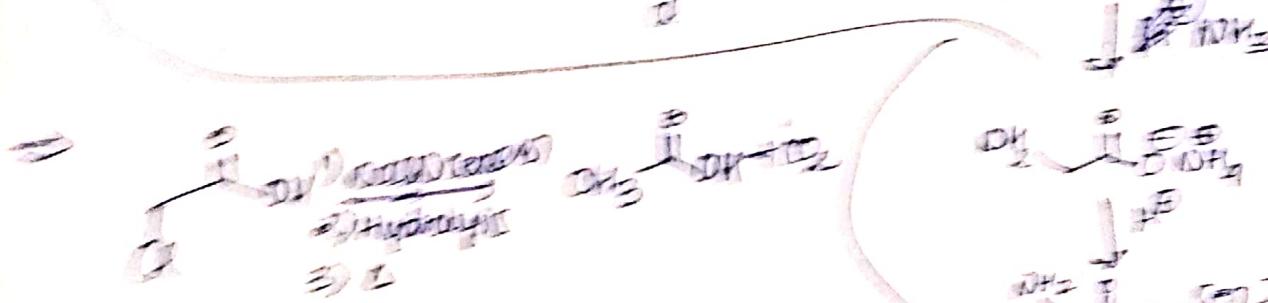




~~One set of α -Hydrogen replaced by α -methyl~~

卷之三

ANSWER
TRUE: Enzyme catalyzed reaction by increasing
Inhalation.

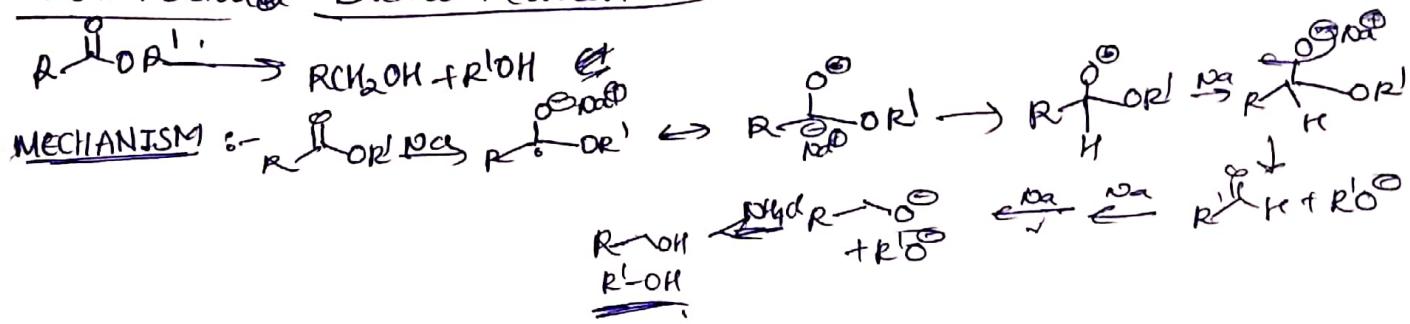


Bordone Hunsicker

→ *Rufous* -



Bouveault-Blanc reduction (Rev)



Esterification and Hydrolysis of Esters (Rev.)

Case (P) In acidic medium,
esterification or Fischer esterification occurs

Case(i) In acidic medium,
esterification or Fischer esterification occurs

Mech.: -

Bimolecular : rate is more for sterically free reacting species -

cond(ii) In basic medium,
 $\text{R}-\text{COOH} + \text{R}'-\text{COO} \xrightarrow{\text{NaOH}}$

Strong - ion

due to already existing strong -ion,
 external Na⁺ doesn't attack carboxyl
 carbon and no esterification takes place.

Expt 3 (iii) Hydrolysis of ester in acidic medium

cond(V) :- 

Step
 A_1^1 / A_1 \Rightarrow acidic medium,
 cleavage of alkoxy bond by unimolecular RDS.

Because of steric factors

$\text{Acid}^{\text{H}} \text{ + } \text{Ester} \xrightarrow{\text{H}_2\text{O}} \text{Alcohol} + \text{Acidic Product}$

$\text{A}^{\text{I}} \text{ Ac} \Rightarrow \text{Acid}^{\text{H}} \text{ + } \text{Acyl bond cleavage by unimolecular RDS.}$

Carey's :- Hydrolysis of ester in basic medium (Saponification rxn).

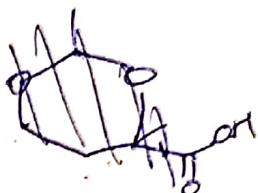
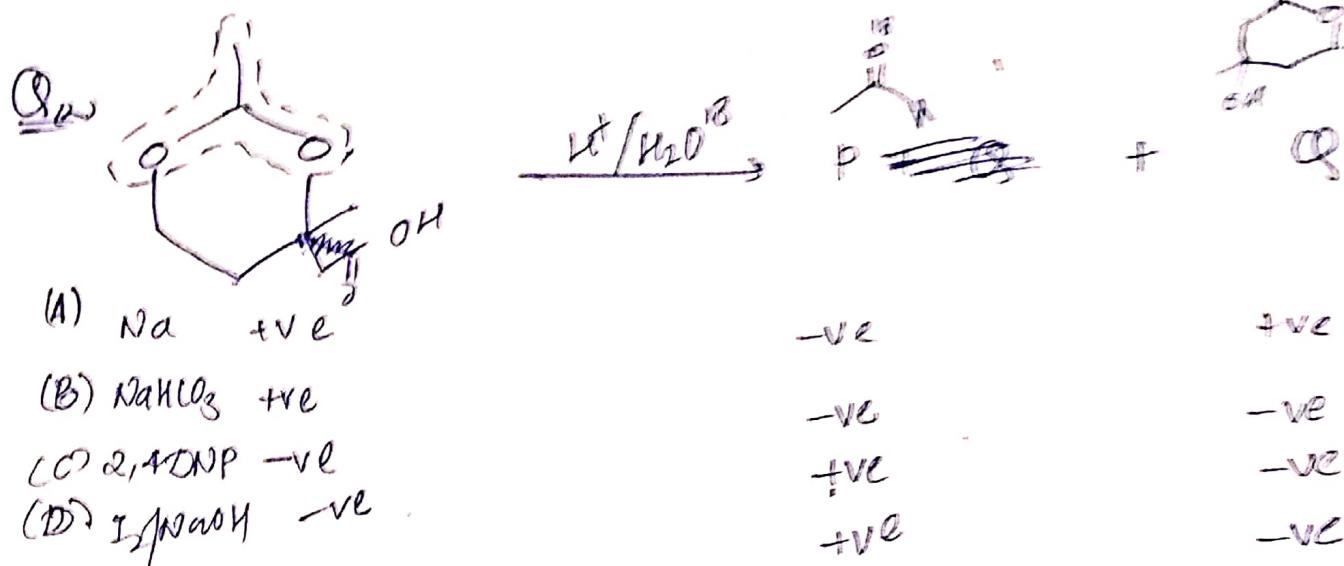
$\text{R}-\overset{\text{OR}}{\underset{\text{RDS}}{\text{O}}} \xrightarrow{\text{OH}^-} \text{R}-\overset{\text{OH}}{\underset{\text{OTs}}{\text{O}}} \xrightarrow{\text{R'-OH}} \text{R}-\overset{\text{OH}}{\underset{\text{O}^+}{\text{O}}} \xrightarrow{\text{H}^+ \text{ transfer}} \text{R'-COO} + \text{R'OH}$

② \Rightarrow Basic medium,

case(vii) → Trans-esterification

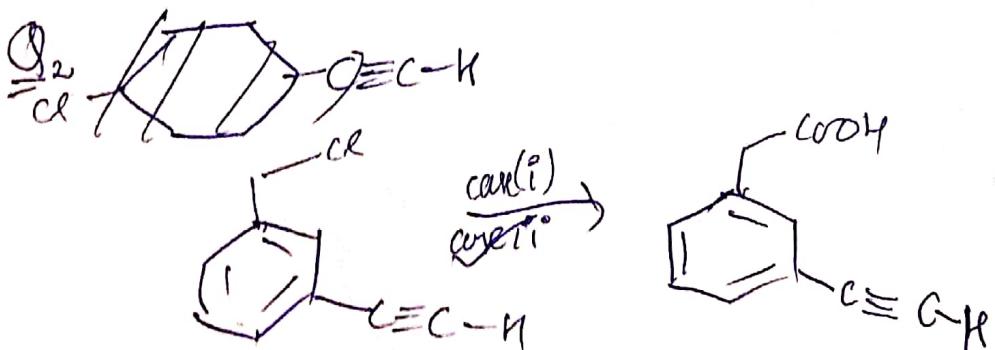
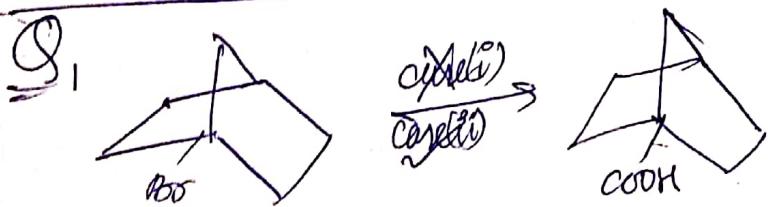
$$R^{\text{I}}\overset{\text{O}}{\underset{\text{C}}{\text{||}}}OR^{\text{I}} + R^{\text{II}}\text{OH} \xrightarrow[\text{OH}^-]{\text{H}^+} R^{\text{I}}\overset{\text{O}}{\underset{\text{C}}{\text{||}}}OR^{\text{II}} + R^{\text{I}}\text{OH}$$

Q_1 (i) $\text{R}-\text{CH}_2-\text{OR}'$ on NaI \rightarrow INERT

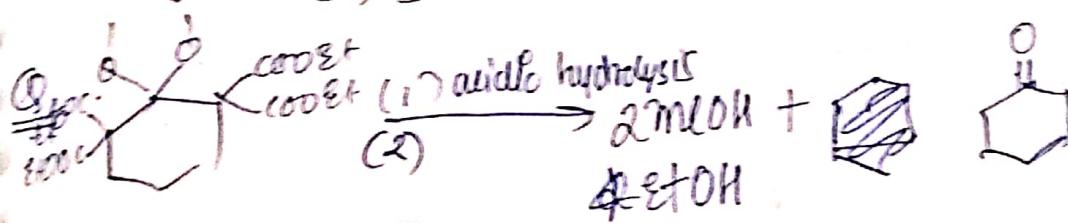
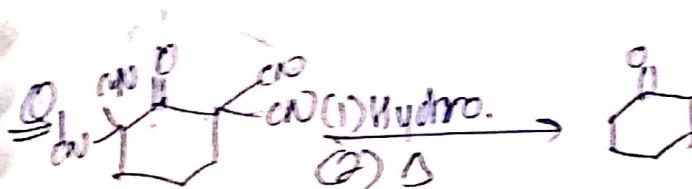
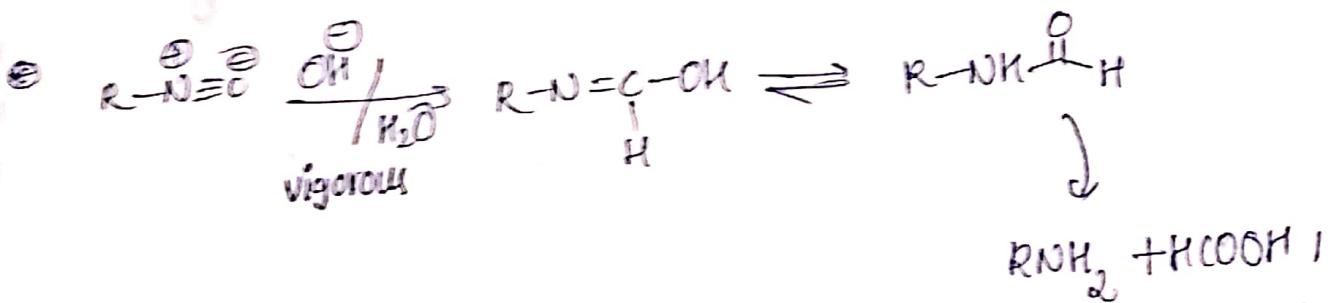
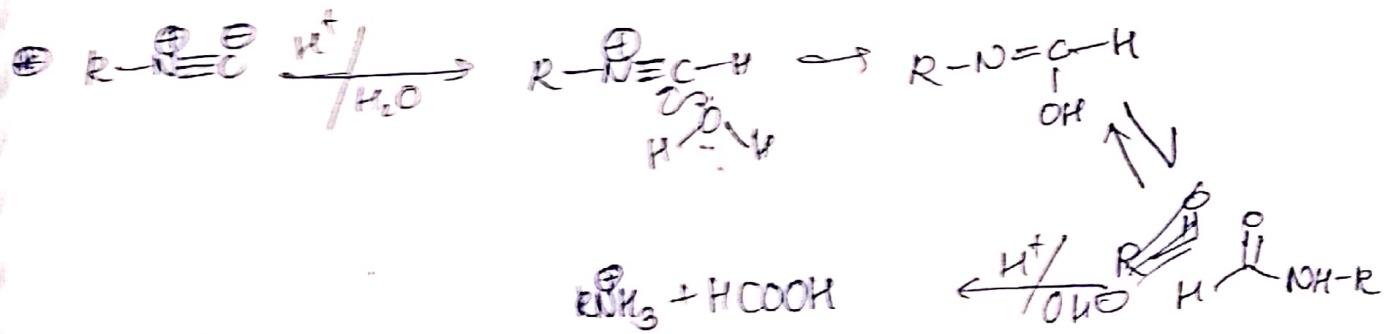
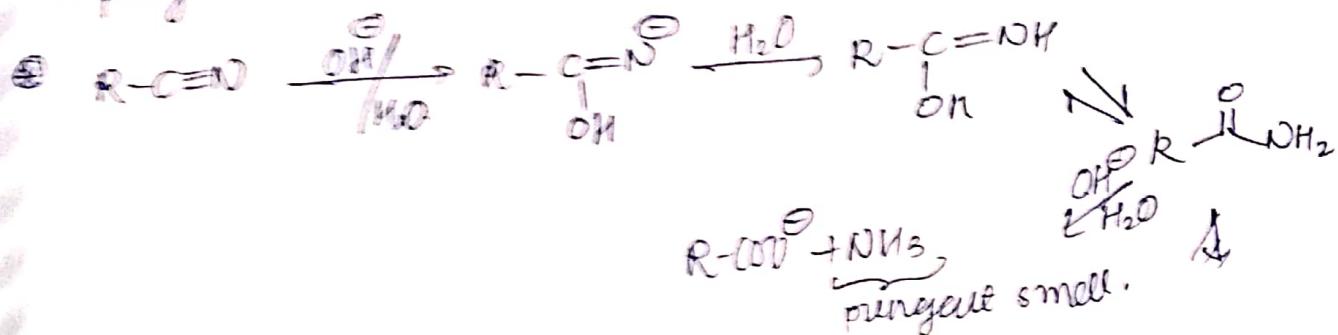


case(i) (i) NaCl
 (ii) Hydrolysis

case(ii) (i) $\text{Mg}/\text{Et}_2\text{O}$
 (ii) Anhydrous solid CO_2 (dry ice)
 (iii) Work up.

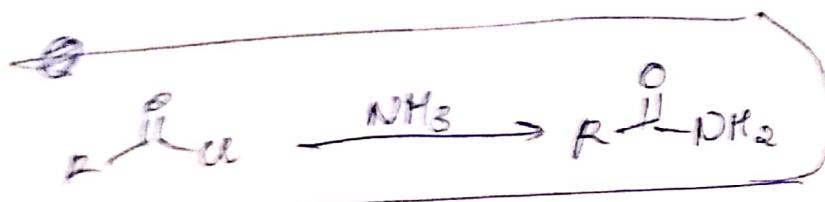


Hydrolysis of nitriles and isocyanides

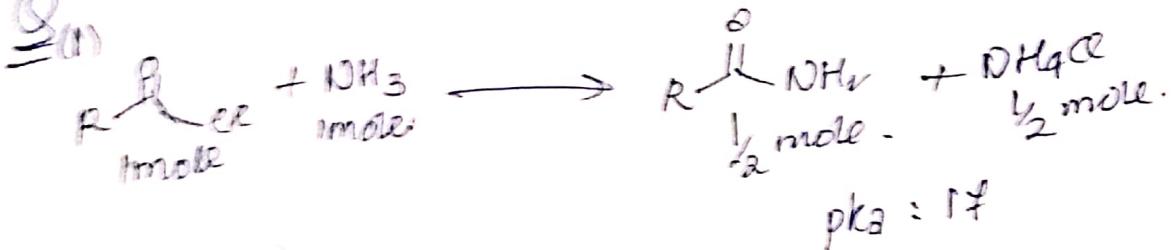


Q no. of isomeric compounds on heating gives

$$(x=6)$$



Q1

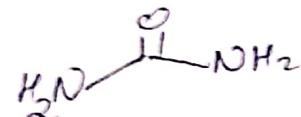


Q2) To convert

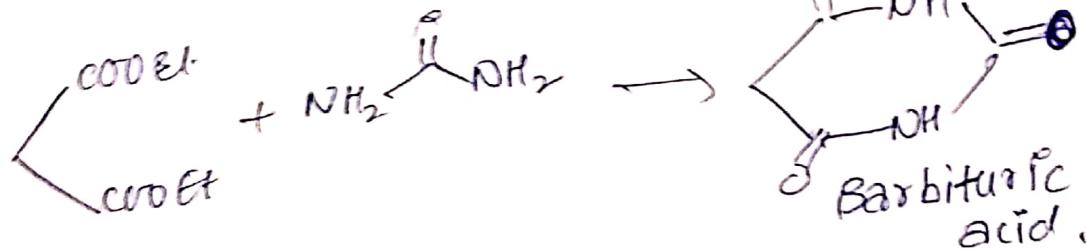
x moles of phosgene



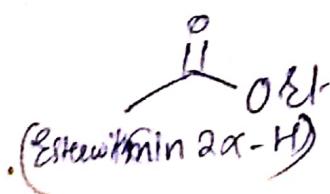
$$\begin{matrix} \text{No. of moles} \\ \text{of NH}_3 \text{ required} \\ = 4x \end{matrix}$$



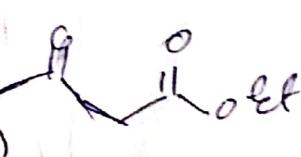
Q3



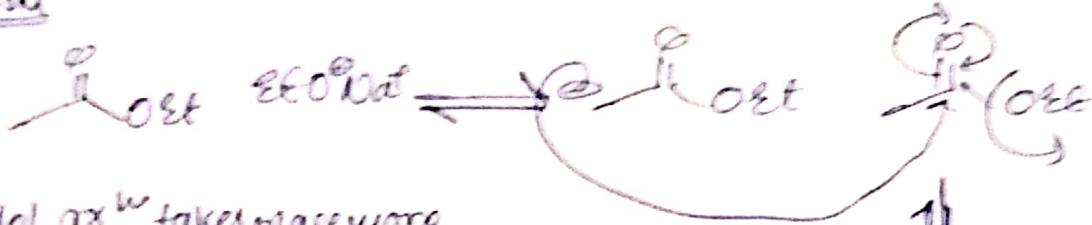
Claisen Rx (or) Condensation



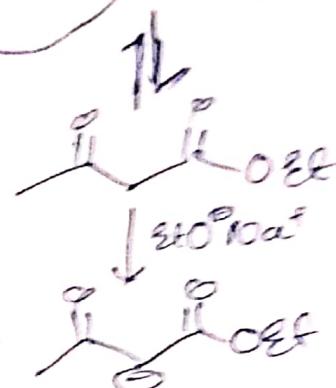
(1) EtO^+Na^+ (excess)
(2) HCl
(Acidification or neutralisation)



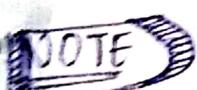
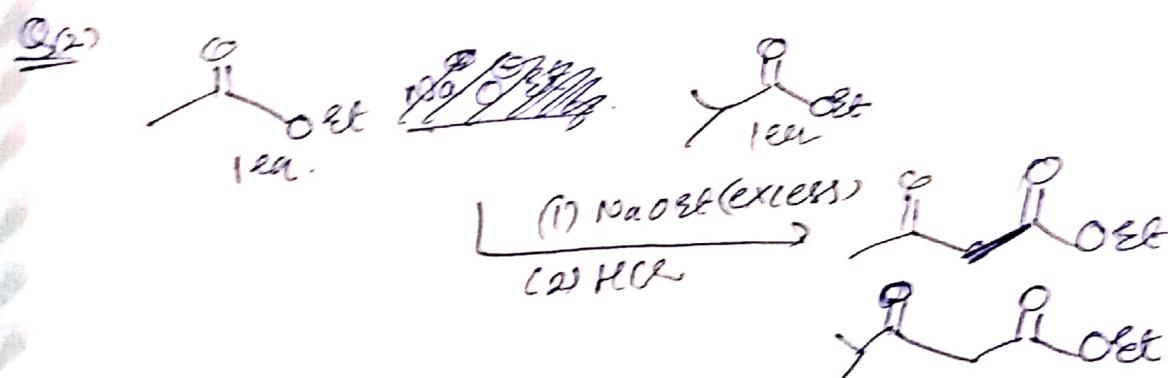
Mechanism



→ Aldol rxn^w takes place more favourably ~~with~~ than Claisen rxn^w.



→ To separate β -keto ester, 2^{nd} α -H is necessary because, due to 2^{nd} -H, enolate ion if formed that is stable and can be isolated by other process.

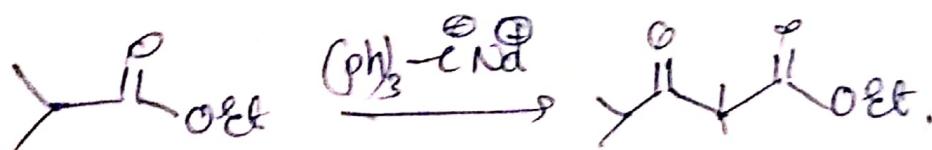


NOTE :- β -keto esters are produced even with one α -hydrogen by means of very strong base.

example

(i) $(\text{Ph})_3\text{C}^+\text{OEt}^-$
strong base
(generates excess quantity of donor)

D



Dieckmann rxn

→ Intramolecular Claisen ester condensation is known as "Dieckmann's cyclisation".

