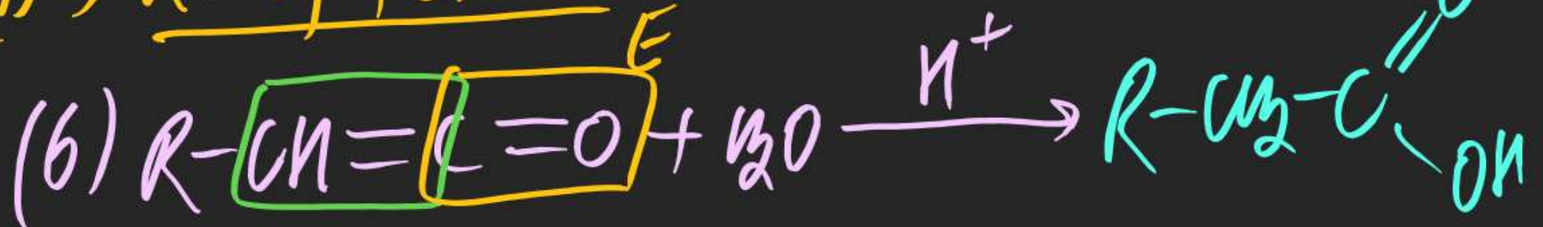
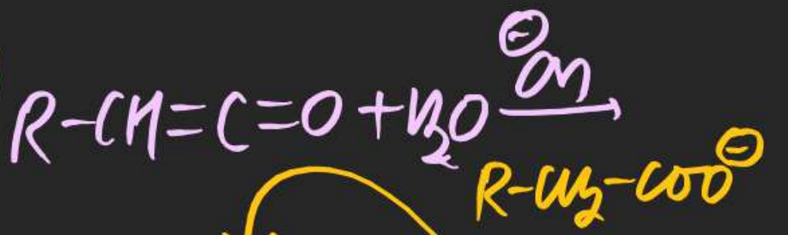
(3) 

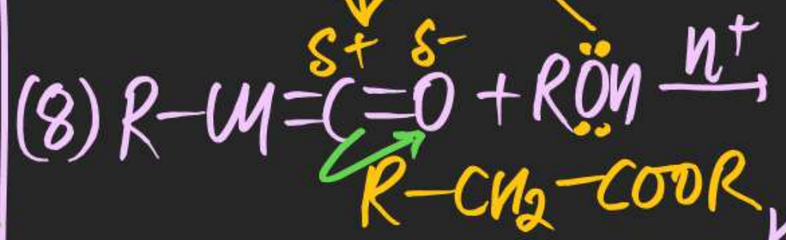
(4) 

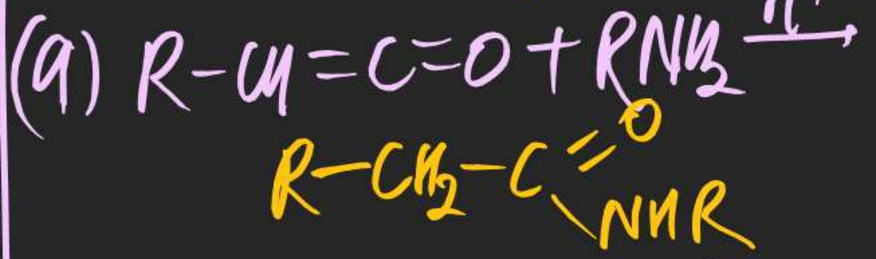
(5) 

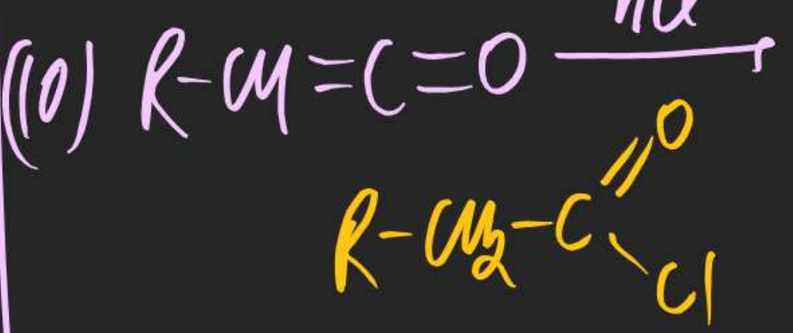
(#) Rxn of Ketene:

(6) 

(7) 

(8) 

(9) 

(10) 

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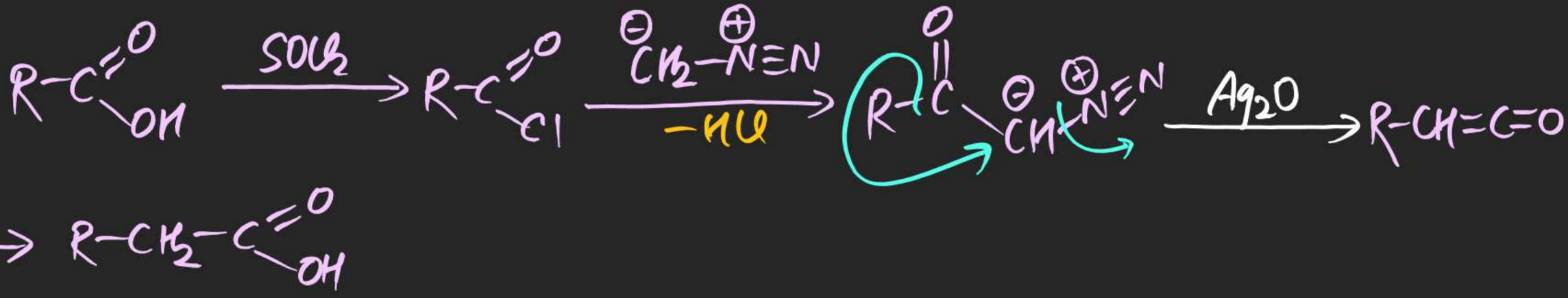
Soln:



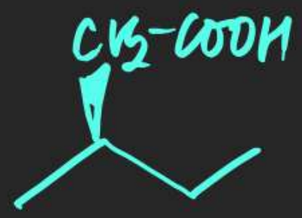
Note (i) Upgradation Rxn

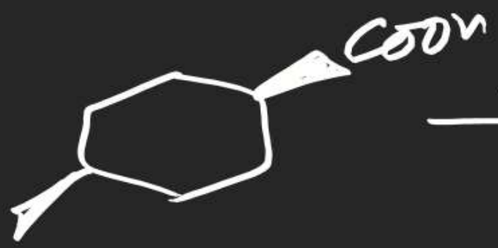
(ii) Configuration never chayes during Reyevent.

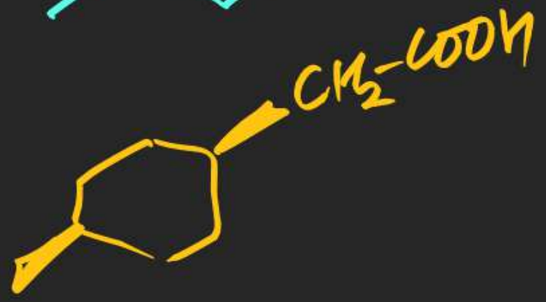
(2) $CH_3-COOH \xrightarrow{\text{''}} CH_3-CH_2-COOH$

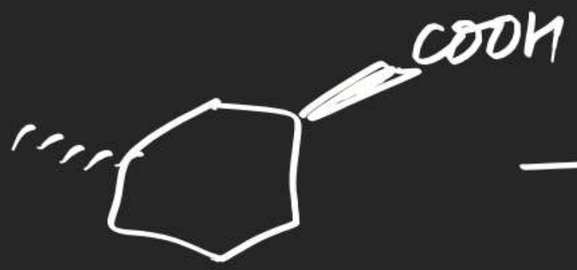
(3) 

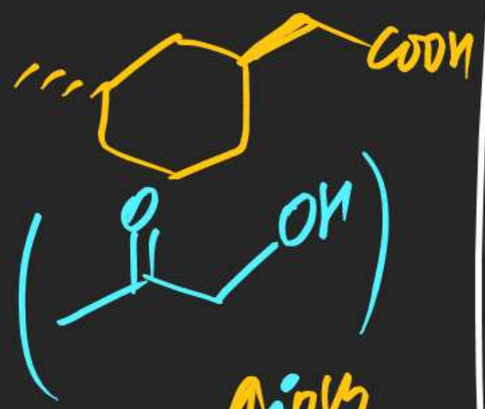
(4) 

(5) 

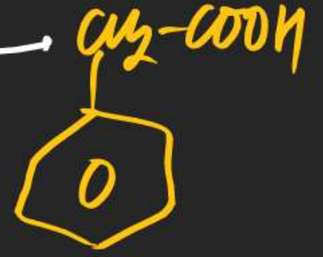



(6) 

(7) $CH_3-COOH \xrightarrow[(ii)\ CH_2N_2]{(i)\ SOCl_2} \underset{(iii)\ H_2O}{\quad}$

(8) 

$\xrightarrow[(ii)\ CH_2N_2]{(i)\ SOCl_2}$ 

$\xrightarrow[(iii)\ H_2O]{(iv)\ Ag_2O}$

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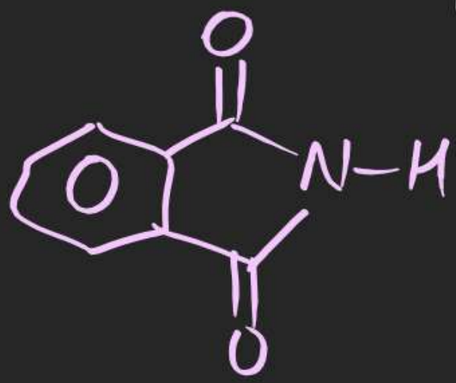
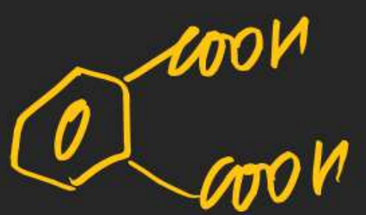
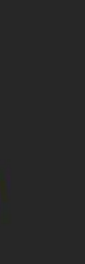
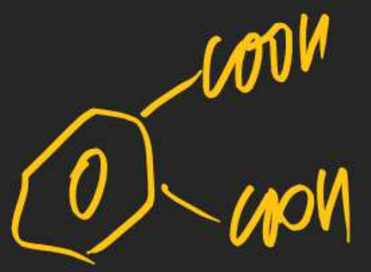
Note (i) Primary Amine formation only.

· R–X must show S_N2 otherwise Required primary Amine is not obtained.

	Primary Amine	
R–X 3°	X	(E^2)
Bridgehead	X	
Aryl C	X	

(2)  $\xrightarrow[\text{(ii) } CH_3-Cl \\ \text{(iii) } H_2O]{\text{(i) KOH}}$ CH_3-NH_2 + 

(3)  $\xrightarrow[\text{(ii) } H-\overset{Me}{\underset{D}{C}}-I \\ \text{(iii) } H_2O]{\text{(i) KOH}}$ $H_2N-\overset{Me}{\underset{D}{C}}-H$ + 

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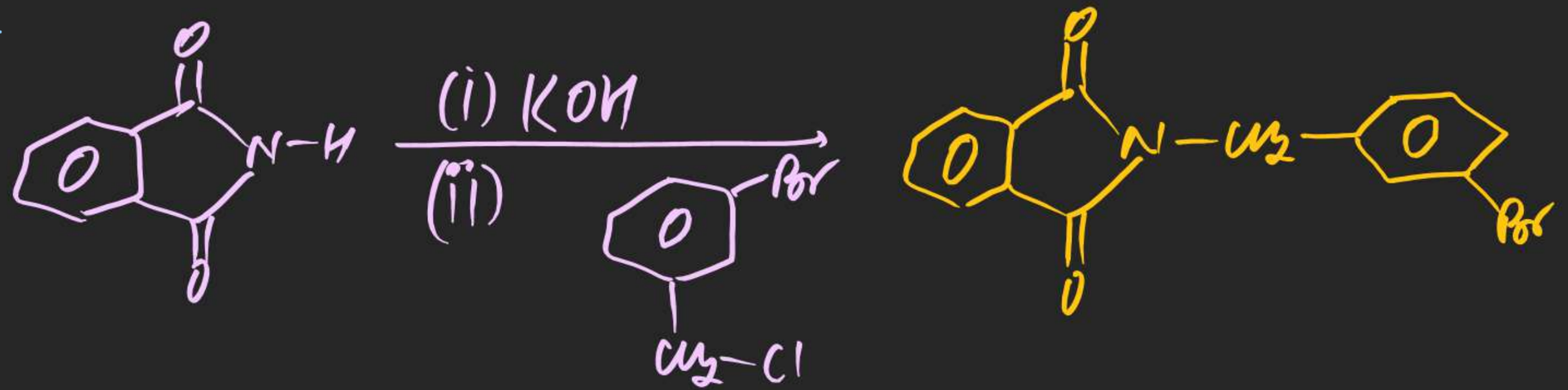
(4) 

(5) which of the following Can be obtained by Gabriel pthalimide synthesis

(i) 1° NH2 ✓

(ii) NH ✗

(iii) 3° NH2 ✗

(iv) NH2 ✗

(v) 1° CH2–NH2 ✓

(vi) NH2 ✗

(vii) NH ✗

(viii) NH ✗

2

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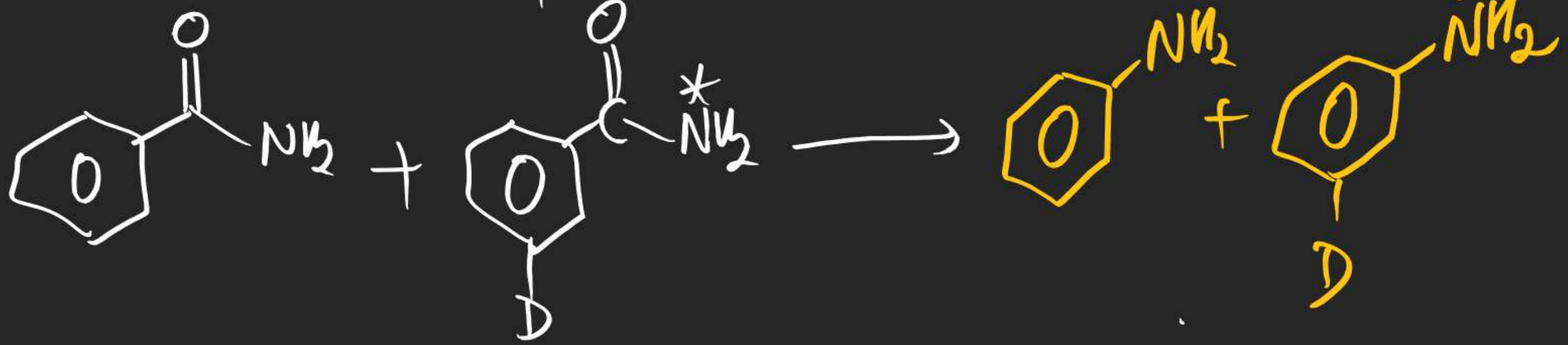
(2) $CH_3-C(=O)-NH_2 \xrightarrow{Br_2+KOH}$ CH_3-NH_2

(3)  →

(4) 

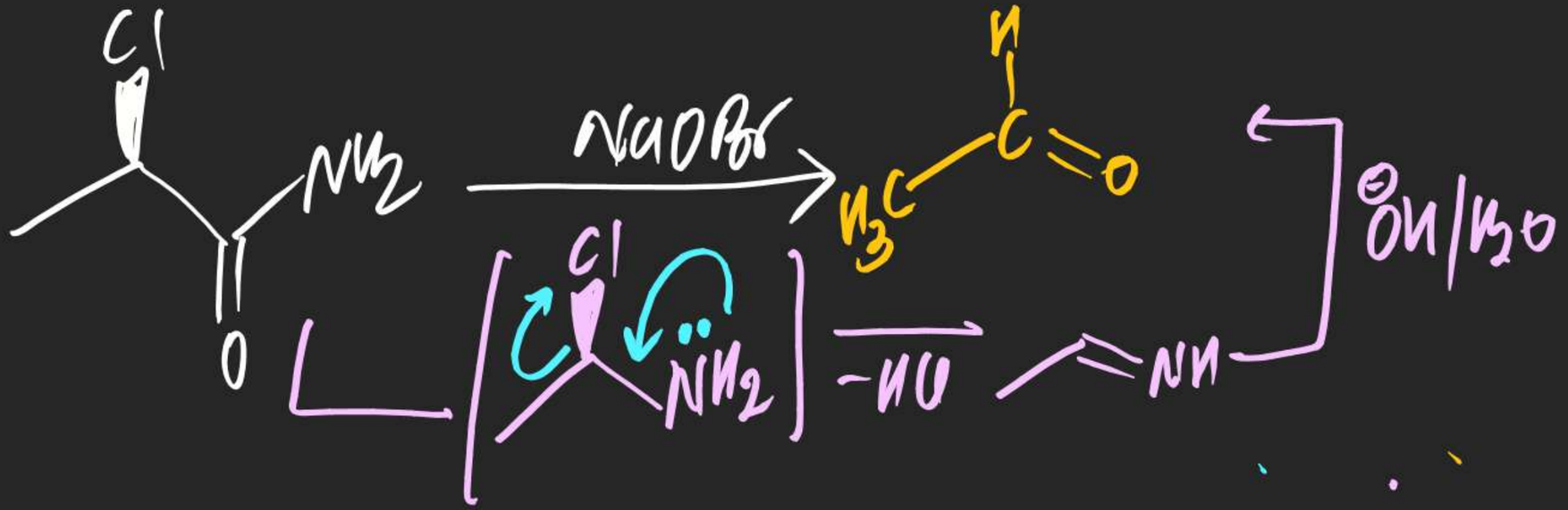
III

(5) 

(6) $CH_3-C(=O)-NH_2 + Br_2 + 4KOD \longrightarrow CH_3-ND_2$

(7) $CH_3-C(=O)-ND_2 + Br_2 + 4KOH \longrightarrow CH_3-NH_2$

(8) $CH_3-C(=O)-ND_2 + Br_2 + 4KOD \longrightarrow CH_3-ND_2$

(9) 

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(10) $Ph-CH=CH-\underset{\underset{O}{\|}}{C}-NH_2 \xrightarrow[Br_2]{NaOH} Ph-CH_2-CH=O$

$\uparrow H_2O/\bar{O}H$

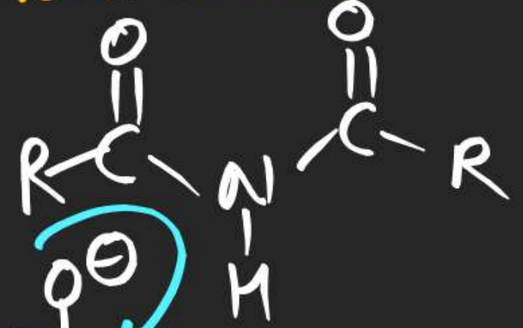
$\rightarrow [Ph-CH=CH-NH_2 \rightleftharpoons Ph-CH_2-CH=NH]$

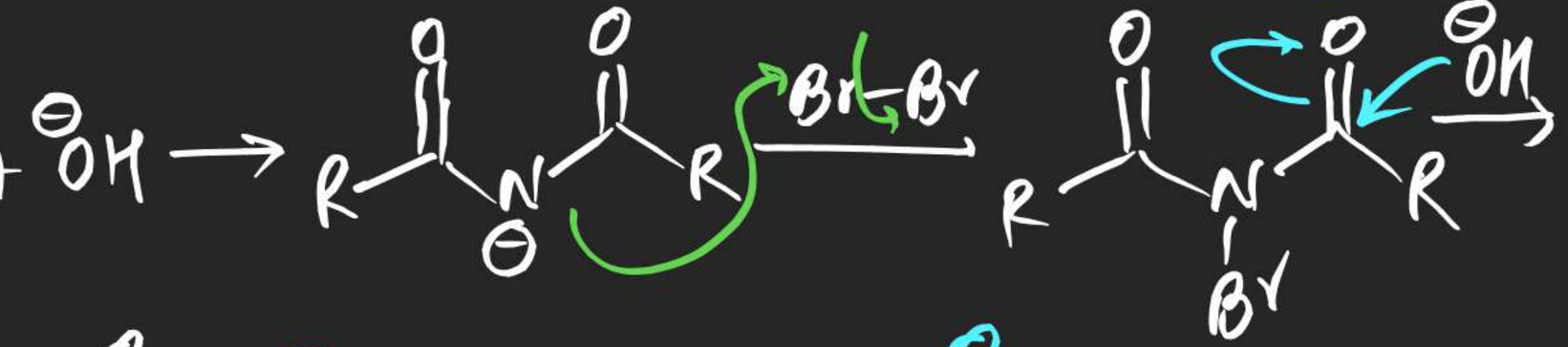
Enamine

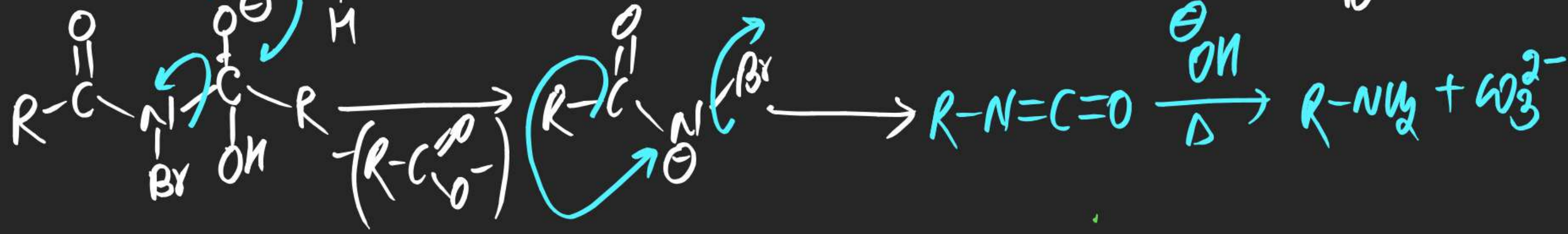
(11)  $+ Br_2 + 5KOH \longrightarrow R-NH_2 + R-COOK + K_2CO_3 + 2KBr + 2H_2O$

Acid Imide

Mechⁿ :







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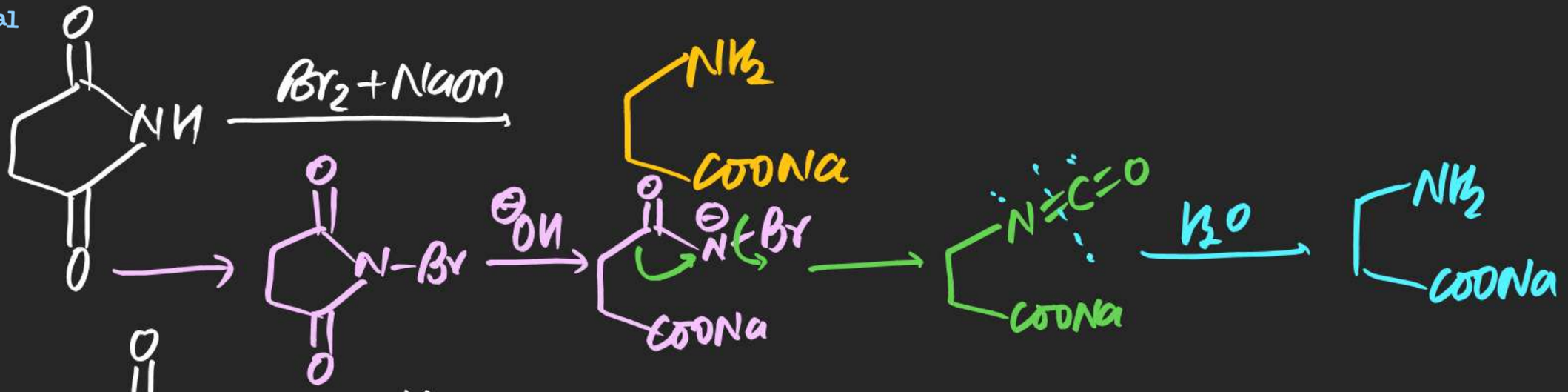
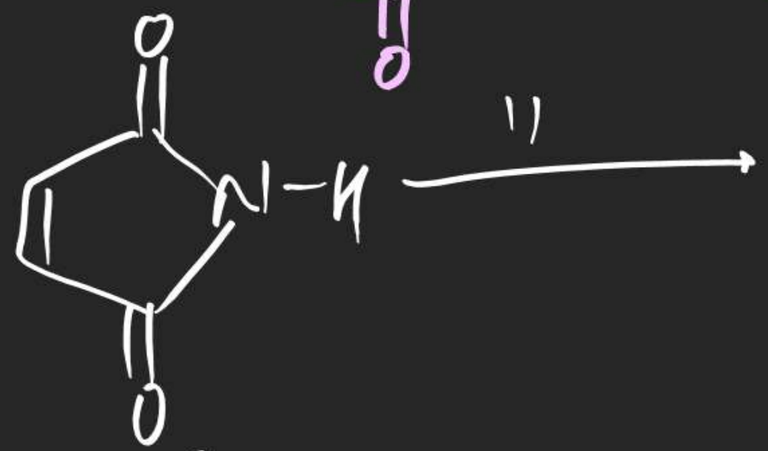
(12)



(13)



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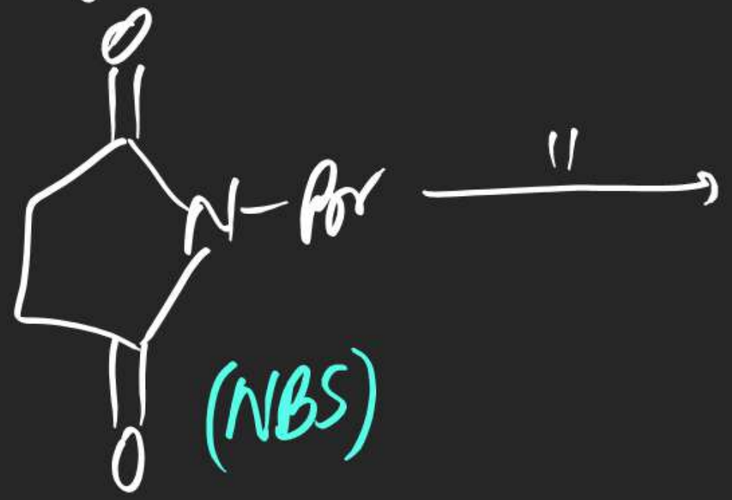
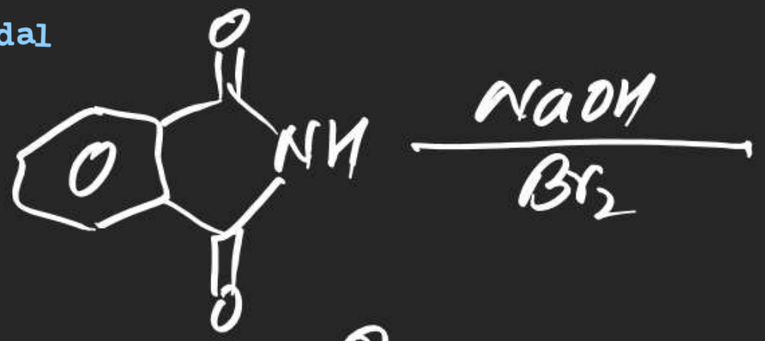
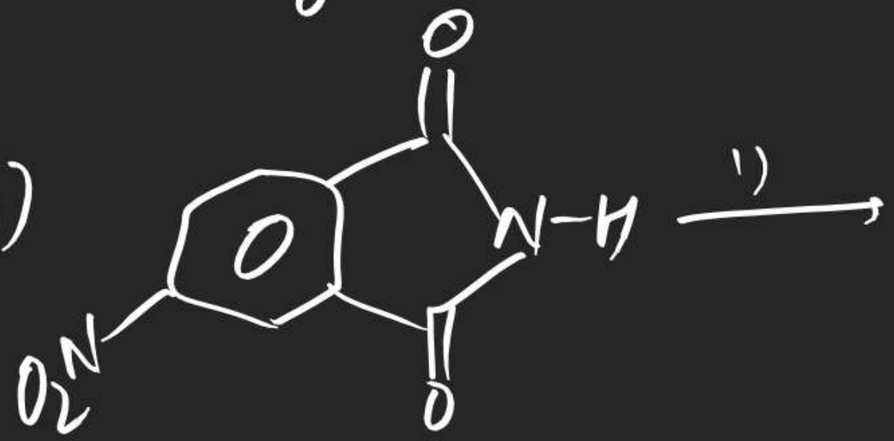
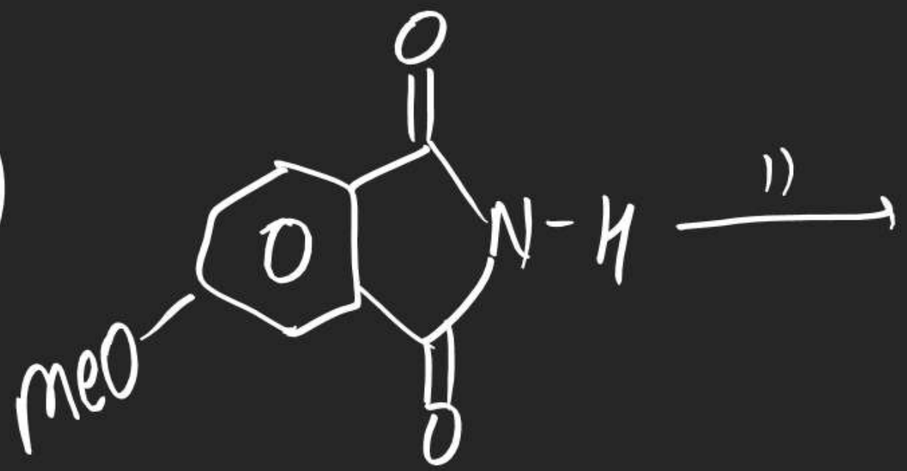
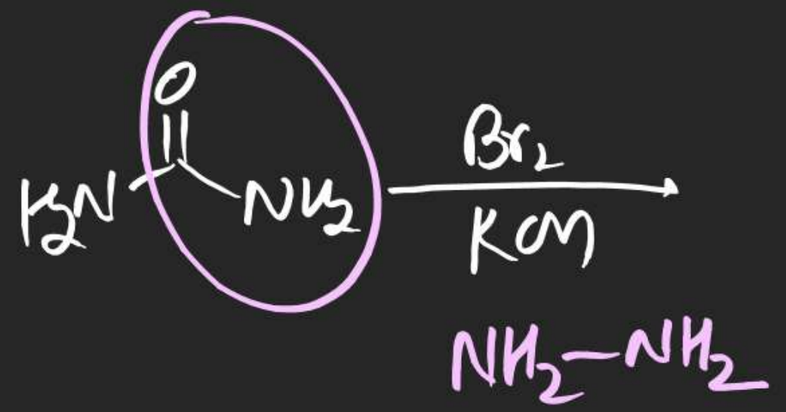


(15) 

(16) 

(17) 

(18) 

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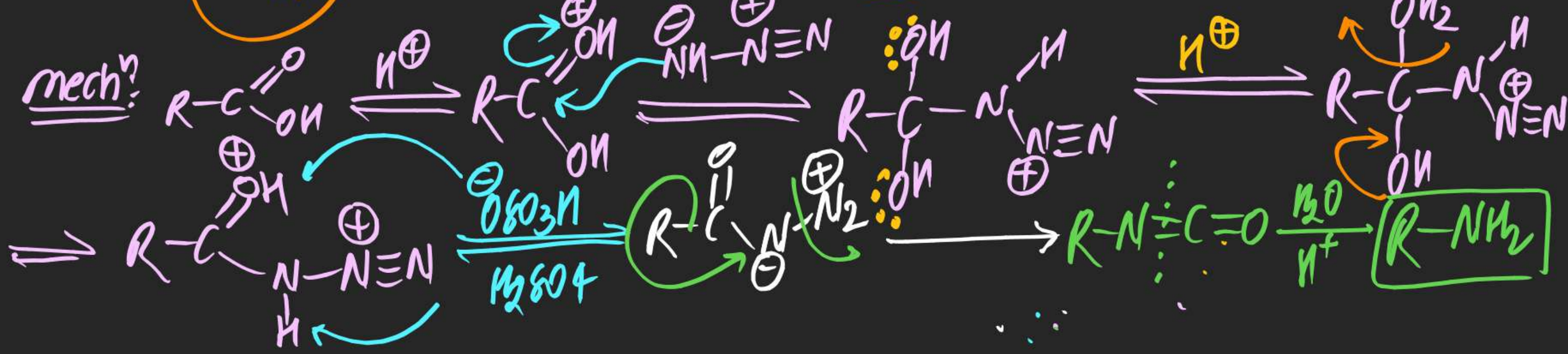
(#) Schimidt Rxn :

⟹ This Rxn is shown By Carboxylic Acid, Ketone & Aldehyde.

(i) For Carboxylic Acid :

⟹ R-COOH on Rxn with Hydrazoic Acid in presence of H_2SO_4 gives primary Amine as a Product.

(1) $R-C(=O)-OH + HN_3 \xrightarrow{H_2SO_4} R-NH_2$



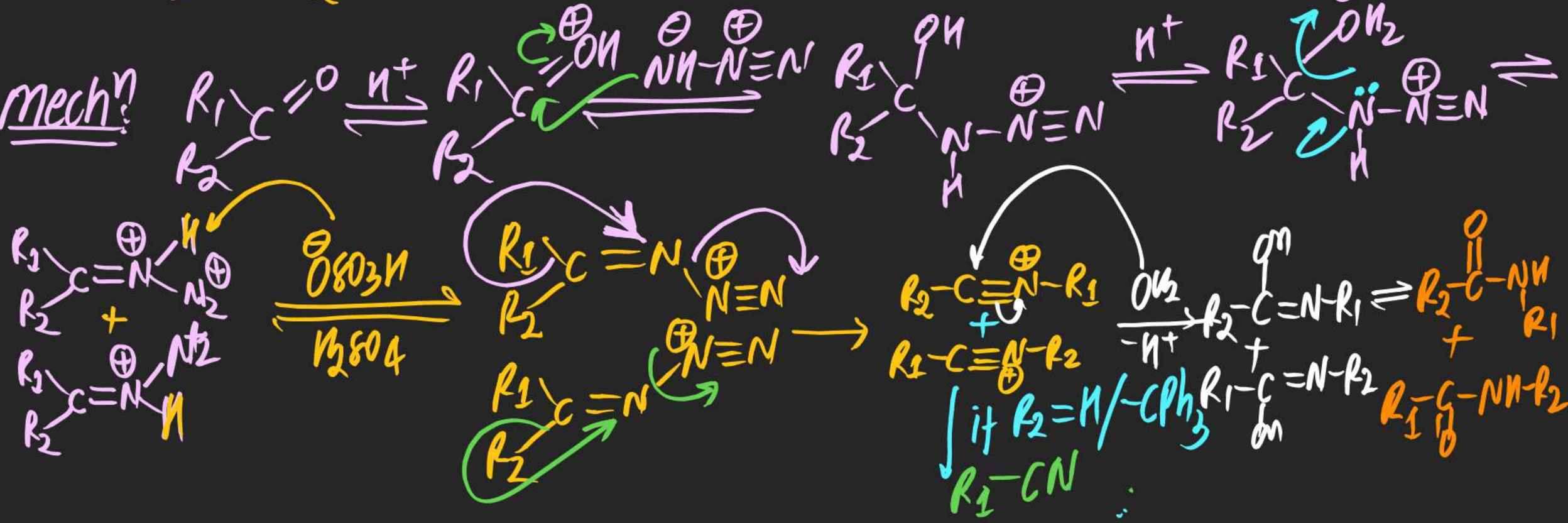
(iii) For ketone:

⇒ ketone on Reaction with HN_3/H_2SO_4 gives Sec-Acid amide as a product.

(2) 

(3) 

Mech^n:



(#) For Aldehyde:

$\Rightarrow$ Aldehyde gives cynide with HN_3/H_2SO_4

(4) 

Note (i) Rearrangement step is r.d.s

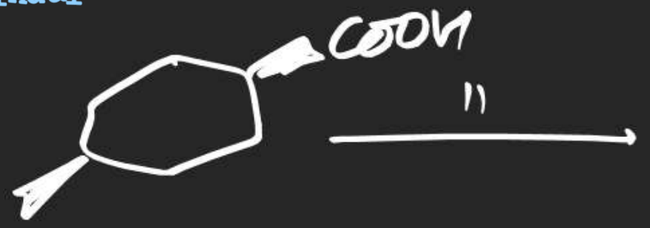
(ii) Configuration never chyes during Rearrangement

(iii) Rearrangement is intramolecular.

(iv) Degradation Rxn in case of Schimidt of Acid group.

(5) $CH_3-CH_2-COOH \xrightarrow[H_2SO_4]{HN_3}$

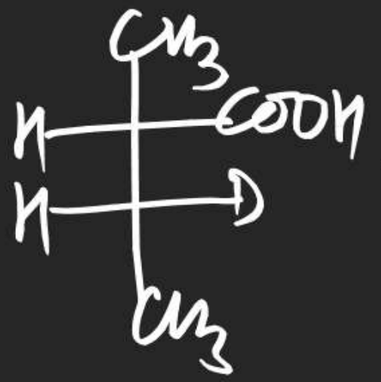
(6) 

(7) 

$\xrightarrow{\text{''}}$

(8) 

$\xrightarrow{\text{''}}$

(9) 

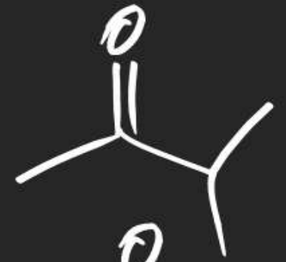
$\xrightarrow{\text{''}}$

(10) 

$\xrightarrow{\text{''}}$

(11) 
$\xrightarrow[H_2SO_4]{HN_3}$

(12) 
$\xrightarrow{\text{''}}$

(13) 
$\xrightarrow{\text{''}}$

(14) 

$\xrightarrow{\text{''}}$

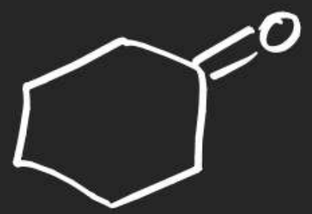
(15) 

$\xrightarrow{\text{''}}$

(16) 

$\xrightarrow{\text{''}}$

M.Imp

(17)  $\xrightarrow[H_2SO_4]{N_3H}$ Product $\xrightarrow[\Delta]{H_2O/H^+}$ Polymer

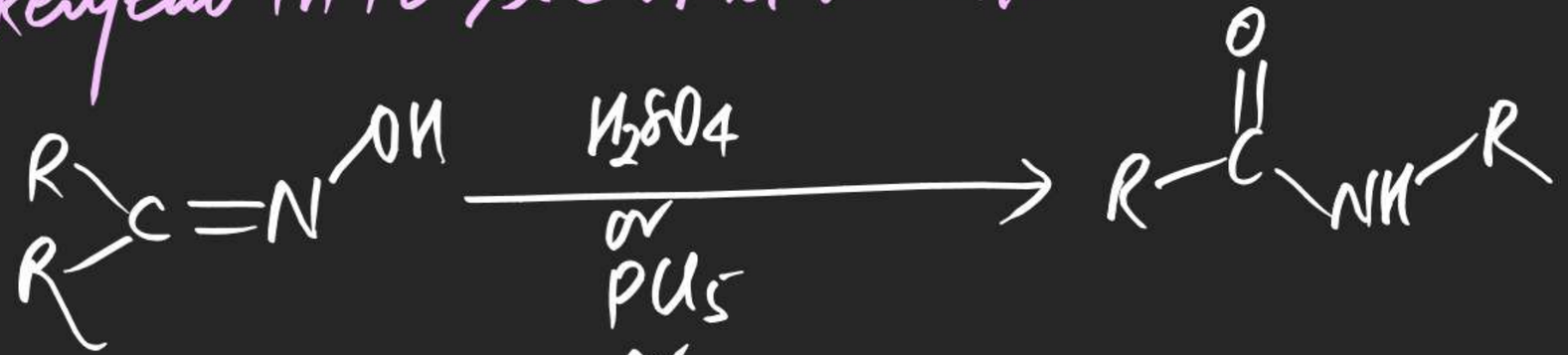
(18) $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[H_2SO_4]{N_3H}$

(19) $CH_3-\overset{O}{\overset{\|}{C}}-CPh_3 \xrightarrow{''} P + Q$

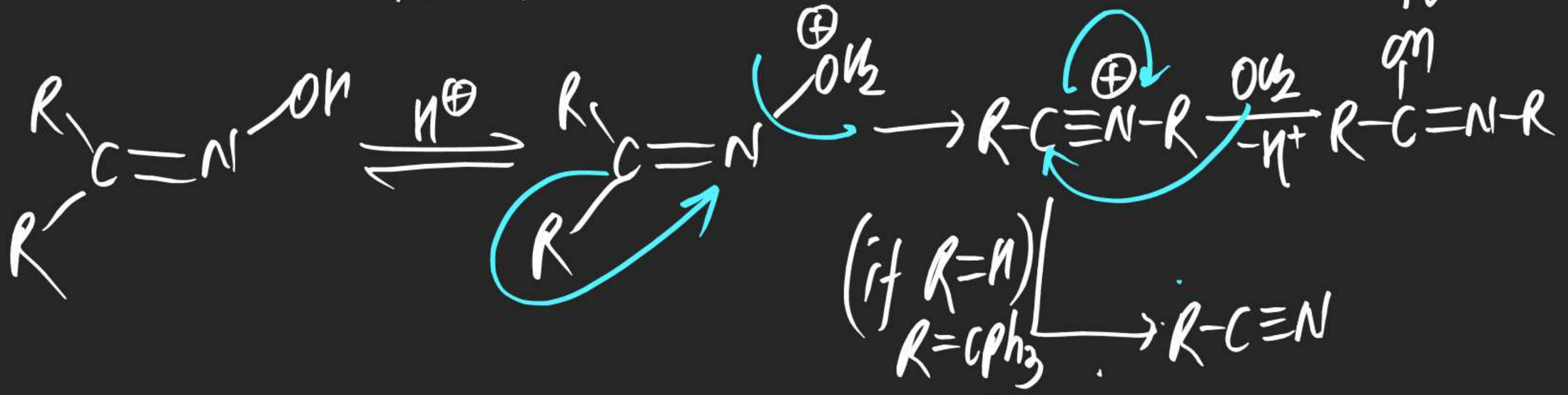
(20)  $\xrightarrow[H_2SO_4]{N_3H}$

(#) Beckmann's Rearrangement:

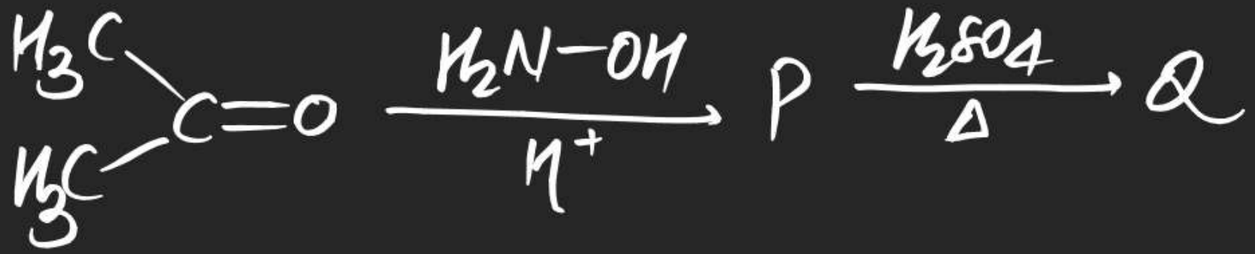
⇒ Whenever oximes are treated with H_2SO_4 / PCl_5 / $KHSO_4$ ..... it Rearrangement into sec. Acid Amide.

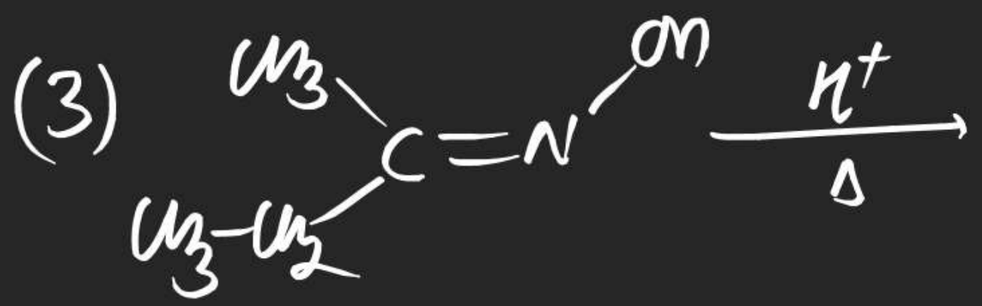
(1) 

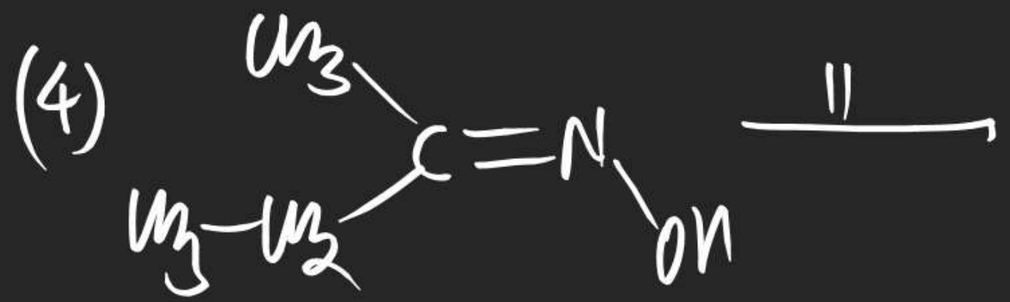
mechⁿ:

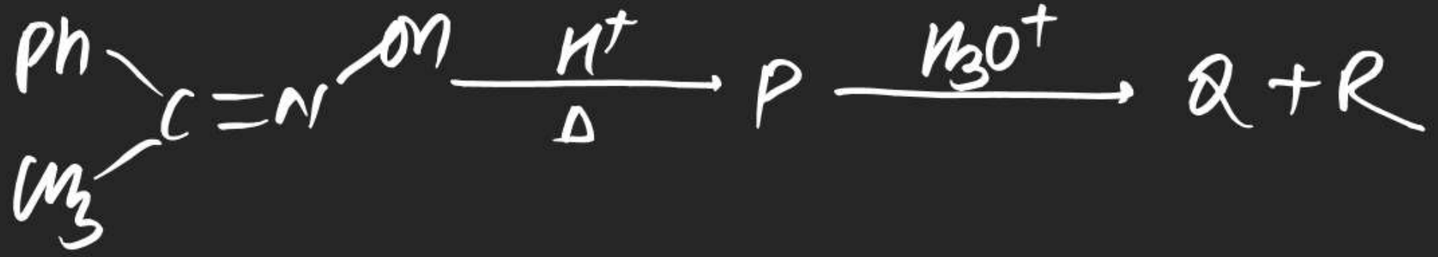


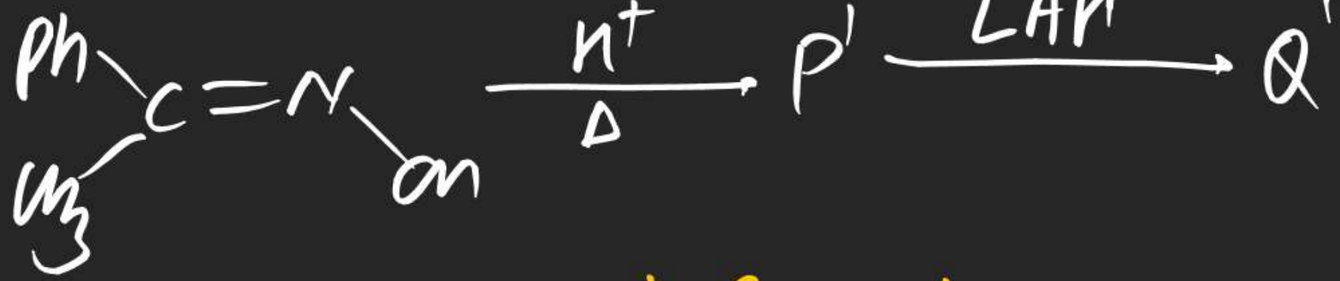
Note (i) Anti group migration takes place.

(2) 

(3) 

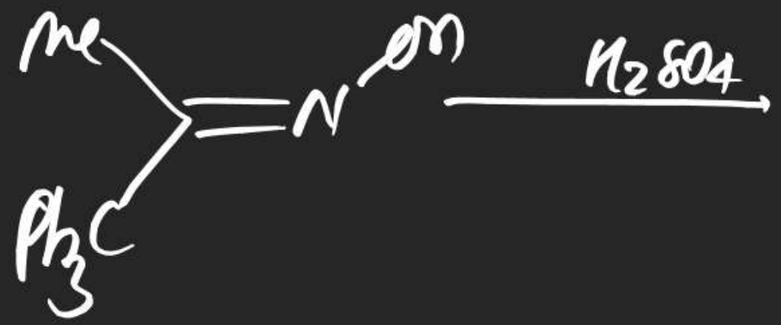
(4) 

(5) 

(6) 

(#) Abnormal Beckmann's Rearrangement.

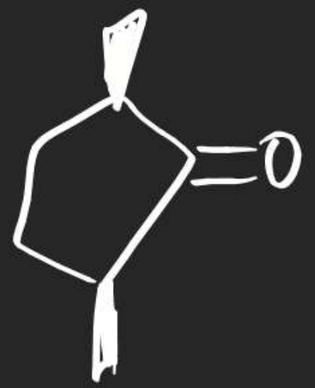
(7) 

(8) 

$\xrightarrow{H_2SO_4}$

(9) 

$\xrightarrow[\Delta]{H^+}$

(10) 

$\xrightarrow{NH_2\text{–}OH}$ P $\xrightarrow[\Delta]{H_2SO_4}$ Q + R

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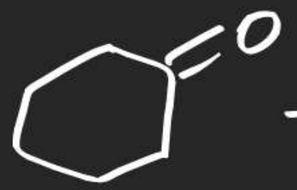
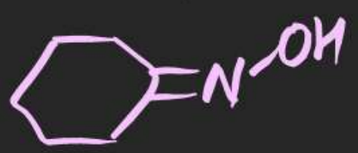
(11)  $\xrightarrow{H_2N\text{-}OH}$ P $\xrightarrow[\Delta]{H_2SO_4}$ Q $\xrightarrow[\Delta]{H_2O}$ "Polymer"

P = 

Q = 

(Caprolectum)

"Polymer" = $+\left[C(=O)-(CH_2)_5-NH\right]_n$ (Nylon-6)

(12) 2° Alcohol $\xrightarrow[H_2SO_4]{Conc.}$ P $\xrightarrow[Zn, H_2O]{O_3}$ Q $\xrightarrow{NH_2\text{-}OH}$ R + S

R $\xrightarrow[\Delta]{H_2SO_4}$ V $\xrightarrow{H_3O^+}$ $CH_3\text{-}COOH$ + W

S $\xrightarrow{PCl_5}$ T $\xrightarrow{H_3O^+}$ U + 

Test for Amines:-

(#) Carbyl Amine Reaction (Isocyanide Test):-

⇒ Sample Containing Primary Amine ($-NH_2$) gives offensive smelling isocyanide in this Test on Reaction with alkaline chloroform.

(1) $R-NH_2 + CHCl_3 + 3NaOH \longrightarrow R-\overset{\oplus}{N}\equiv\overset{\ominus}{C} + 3NaCl + 2H_2O$

mech:-

$H-C(Cl)(Cl)(Cl) + NaOH \longrightarrow Na\overset{\oplus}{C}\overset{\ominus}{Cl_3} + H_2O$

$\Downarrow$

$NaCl + :CCl_2$

(x) DCC (Dichloro Carbene)

(x) Electrophile

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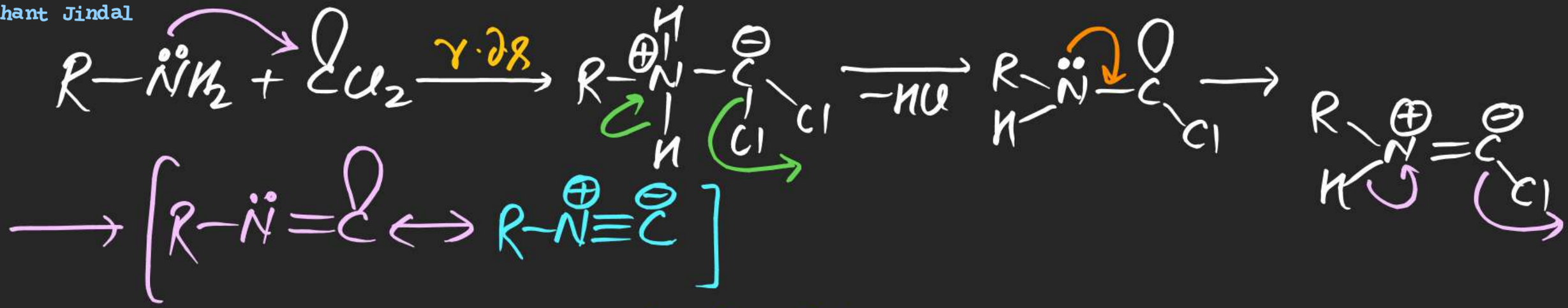

Note (i) CCl_2 (DCC) is electrophile

(ii) Rxn of Amine & DCC is γ-elimination

(iii) Rxn is used in POC for distinguishing of Primary Amine.

(iv) Smell Test

(2) $CH_3-CH_2-NH_2 \xrightarrow{CHCl_3/NaOH}$

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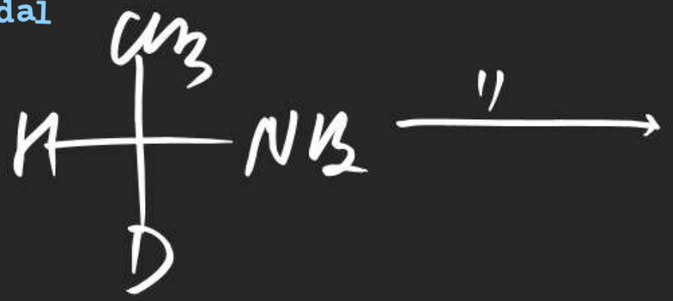
(3) 

$\xrightarrow{\text{''}}$

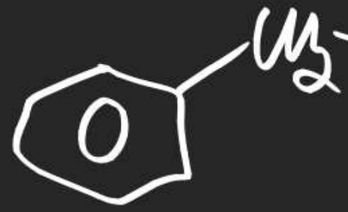
(4) 

$\xrightarrow{\text{''}}$

(5) 

$\xrightarrow{\text{''}}$ P $\xrightarrow{H_3O^+}$ Q + R

R → Tollens reagent (Silver mirror)

(6) 

$\xrightarrow{\text{''}}$

(7) 

Amide
$\xrightarrow{\text{''}}$ X

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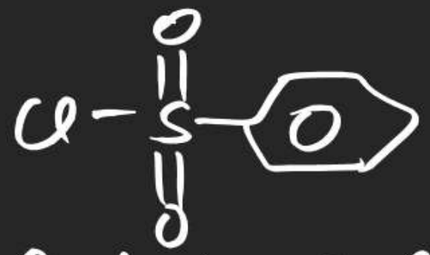
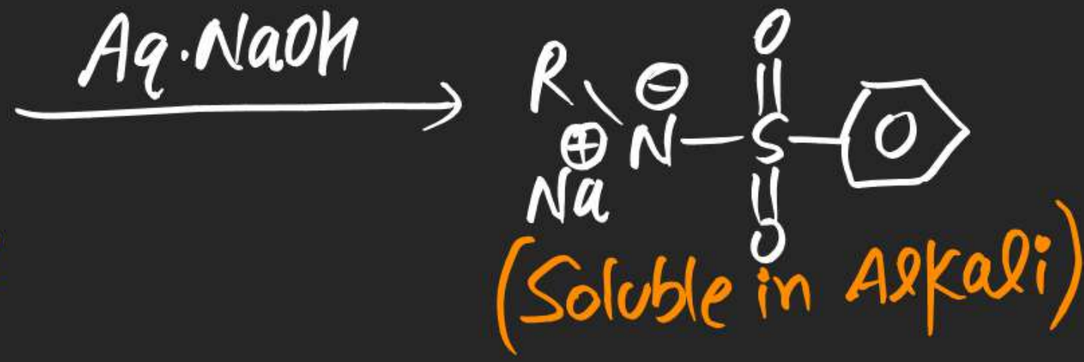
(#) Hinsberg's Test :

⟹ Hinsberg's Regent 

⟹ By this Test 1°, 2° & 3° Amines Can be distinguished & seprated.

(a) $R-NH_2$ Primy Amine  Sec. Sulphonamide  (Soluble in Alkali)

(b) R_2NH Sec. Amine  Tert. Sulphonamide ⟶ Insoluble in Alkali

(C) R_3N ⟶ No Rxn

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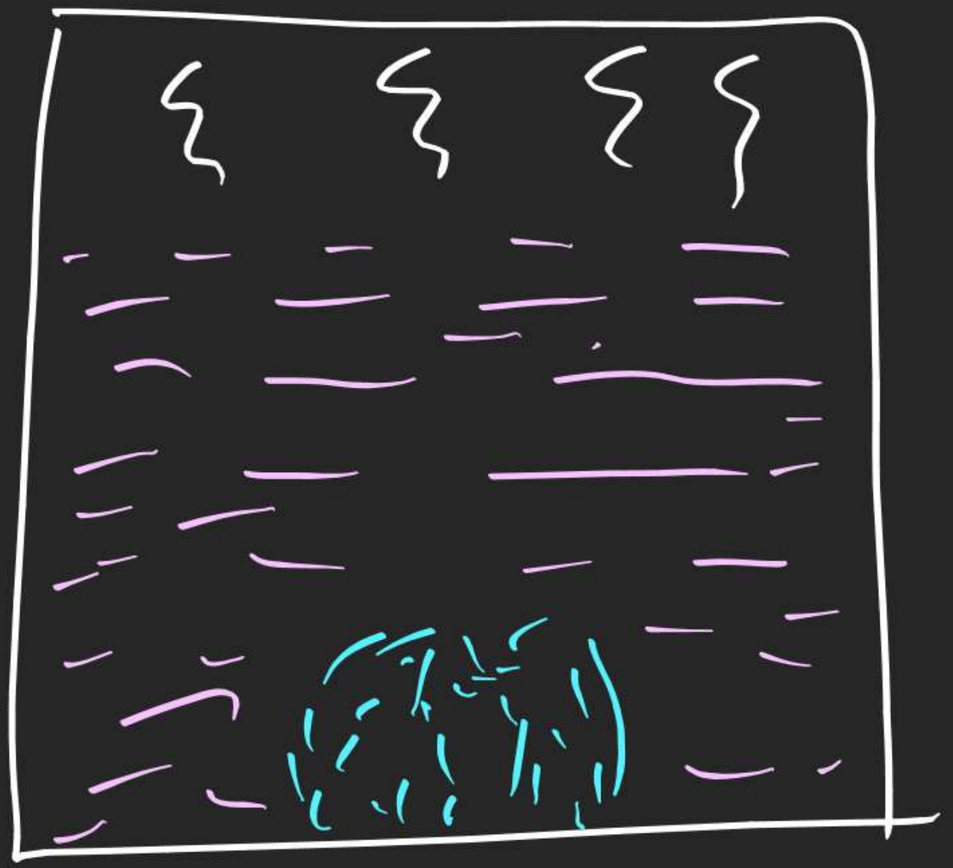
(#) Di Ethyl oxalate Test:

(a) $\begin{matrix}COOEt\\COOEt\end{matrix}$ $+ R_3N \longrightarrow X$

(b) $\begin{matrix}COOEt\\COOEt\end{matrix}$ $+ R_2NH \longrightarrow \begin{matrix}CONR_2\\COOEt\end{matrix}$ Oxamic ester (liquid)

(c) $\begin{matrix}COOEt\\COOEt\end{matrix}$ $+ R-NH_2 \longrightarrow \begin{matrix}CONHR\\|\\CONHR\end{matrix}$ Oxamide (Solid)



Note Test is used for distinguishion & separation of Primary, Sec & Tertiary Amin.

(#) Mustard oil Test :-

⇒ $R-NH_2$ on Reaction with $HgCl_2 + CS_2$ gives mustard oil smelling Compound ($R-NCS$).

$$R-NH_2 + CS_2 + HgCl_2 \longrightarrow \underset{\text{(Alkyl isothiocynate)}}{R-N=C=S} + HgS + 2HCl$$

MIP

(#) Dye Azo Test

⇒ This Test is used for distinguishion b/w aliphatic primary Amine & Aromatic primary Amine.

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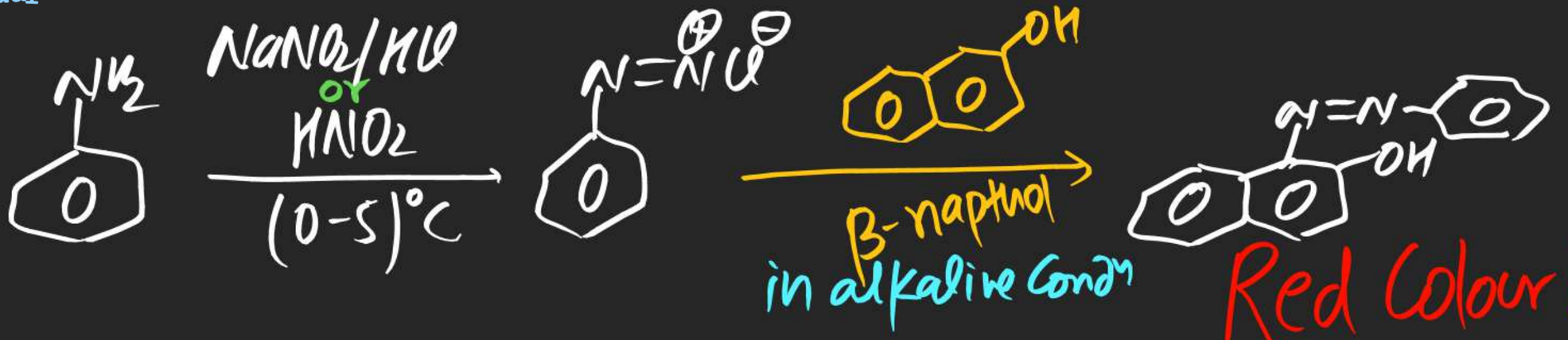
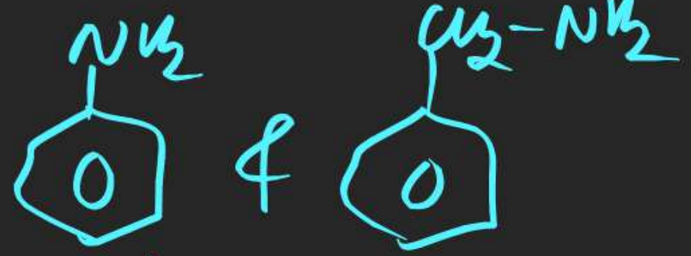
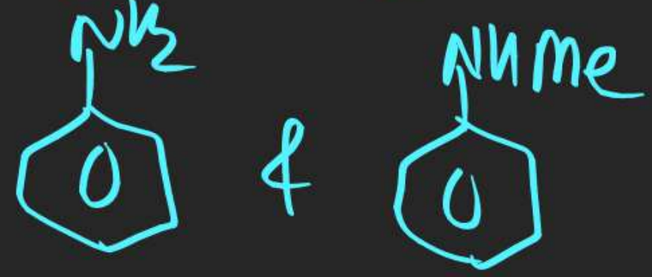
(a) 

(b) 

Note

(a) 

(b) 

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Aromatic Compound