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Amine preparation from 5 step-down :-

1) Hoffmann bromamide Reaction
2) Curtius Reaction
3) Schmidt Reaction
4) Lossen Rearrangement.

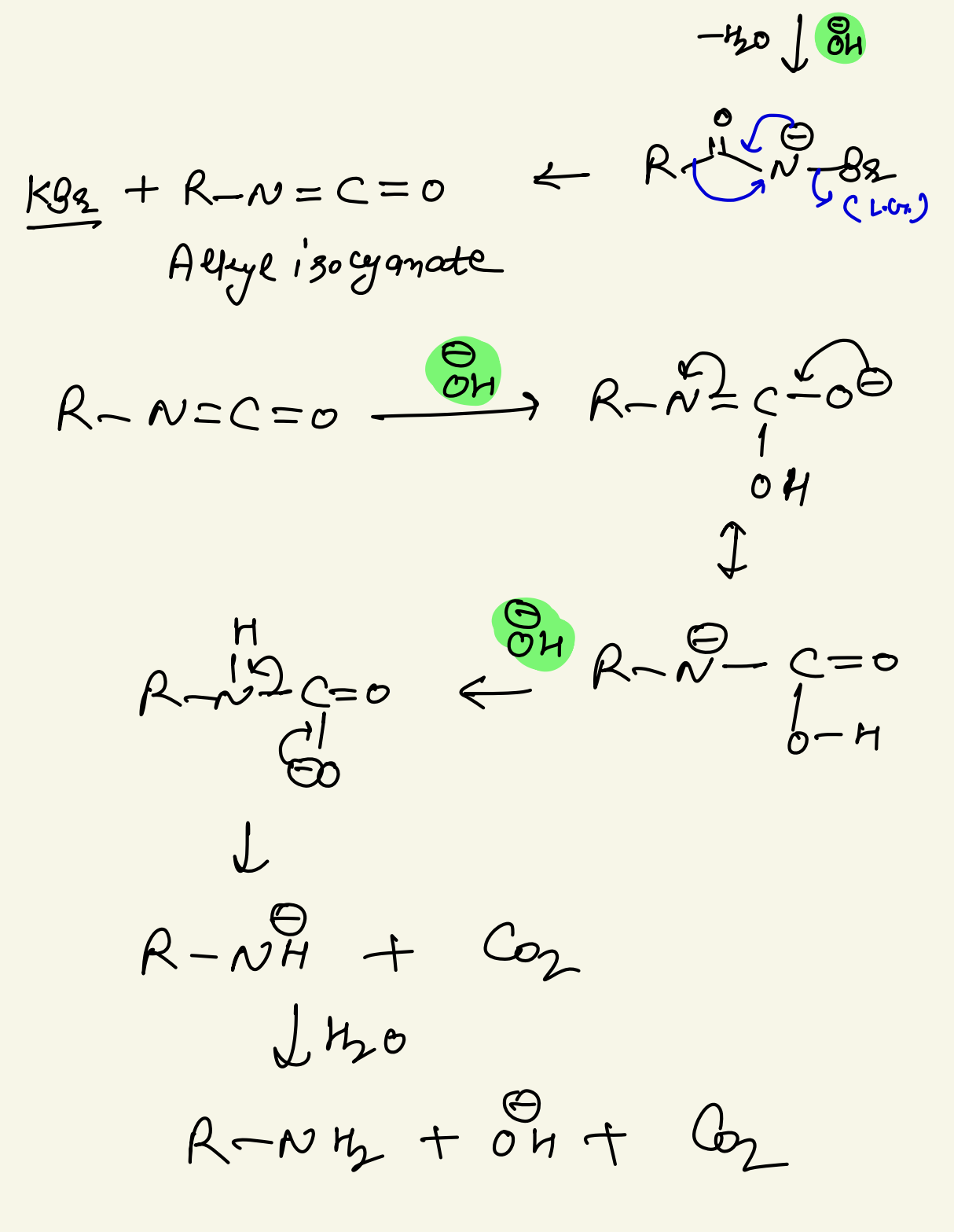
1) Hoffmann bromamide Reaction :-

(i) $R-\overset{O}{\overset{\|}{C}}-NH_2 + 4KOH + 1Br_2 \longrightarrow R-NH_2 + K_2CO_3 + 2KBr + 2H_2O$

1° amide → 1° amine

Mechanism :-

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[-H_2O]{KOH} R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{N}H \xrightarrow{Br_2} R-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-Br$


−H2O
OH
KBr + R−N=C=O
Alkyl isocyanate
(Lossen)
OH
OH
CO2
H2O

Points to be Noted:-

① 1st step is acid-base Rxn.

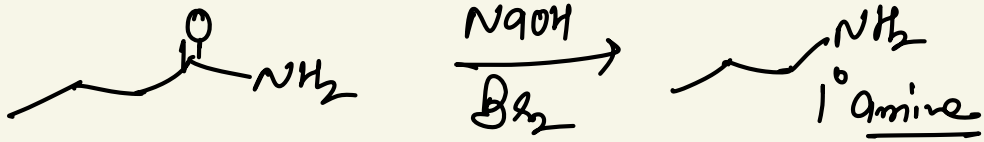
② Br_2 act as an $E^{\oplus}$.

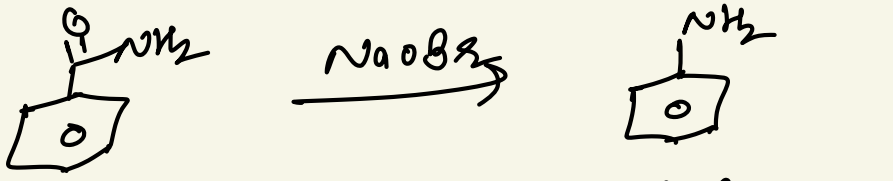
③ Nitrene is formed as an intermediate which cannot be isolated.

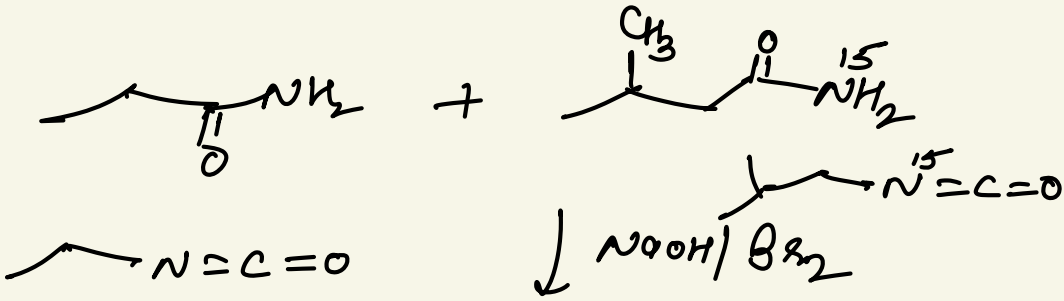
④ ** Step down Rxn.

⑤ Used for preparation of 1° amine from 1° amide.

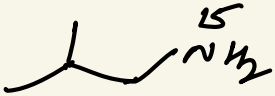
⑥ 2° or 3° amide doesn't give amine from this Rxn

Q. 

Q. 

Q. 

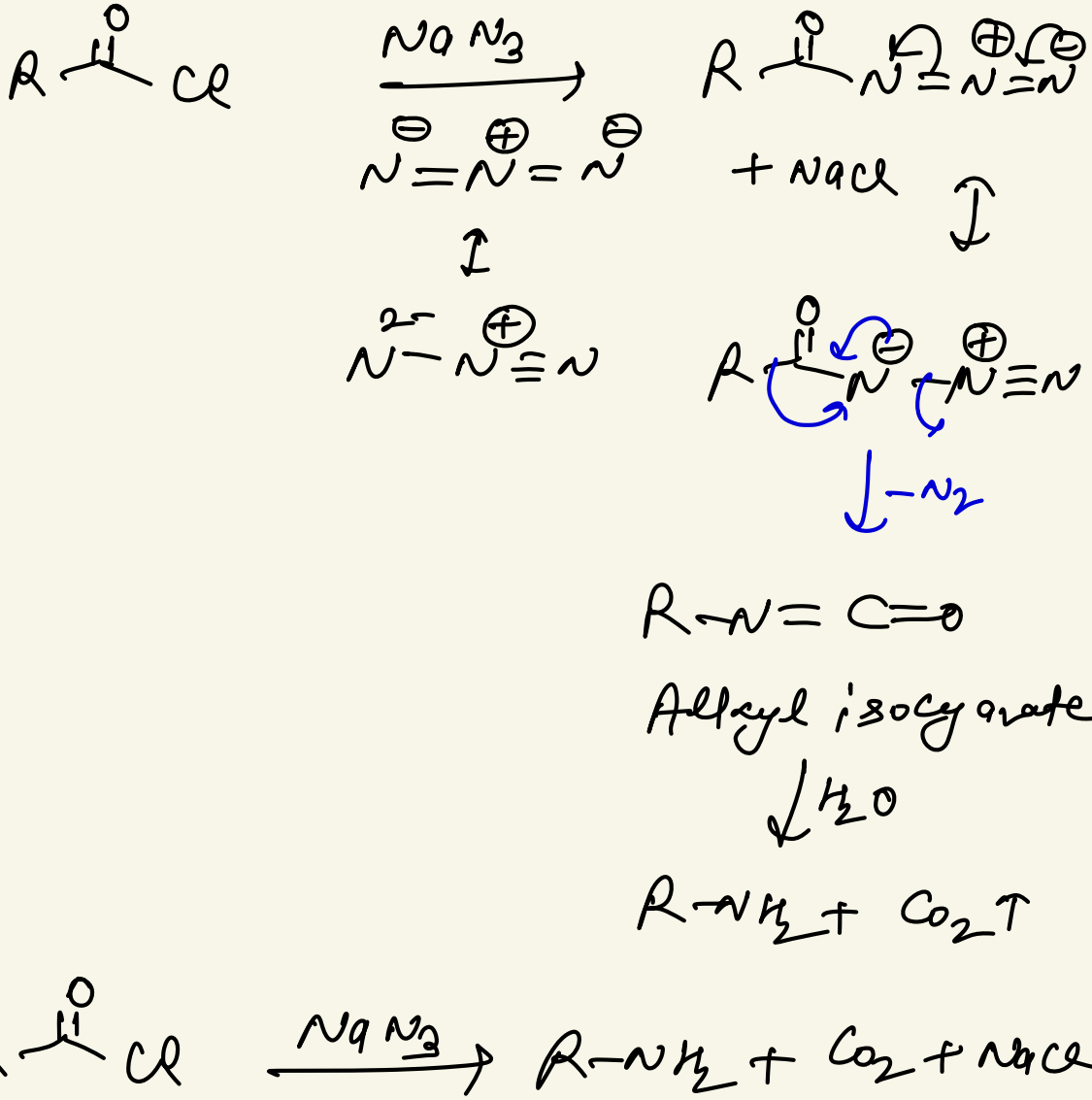
a) 

b) 

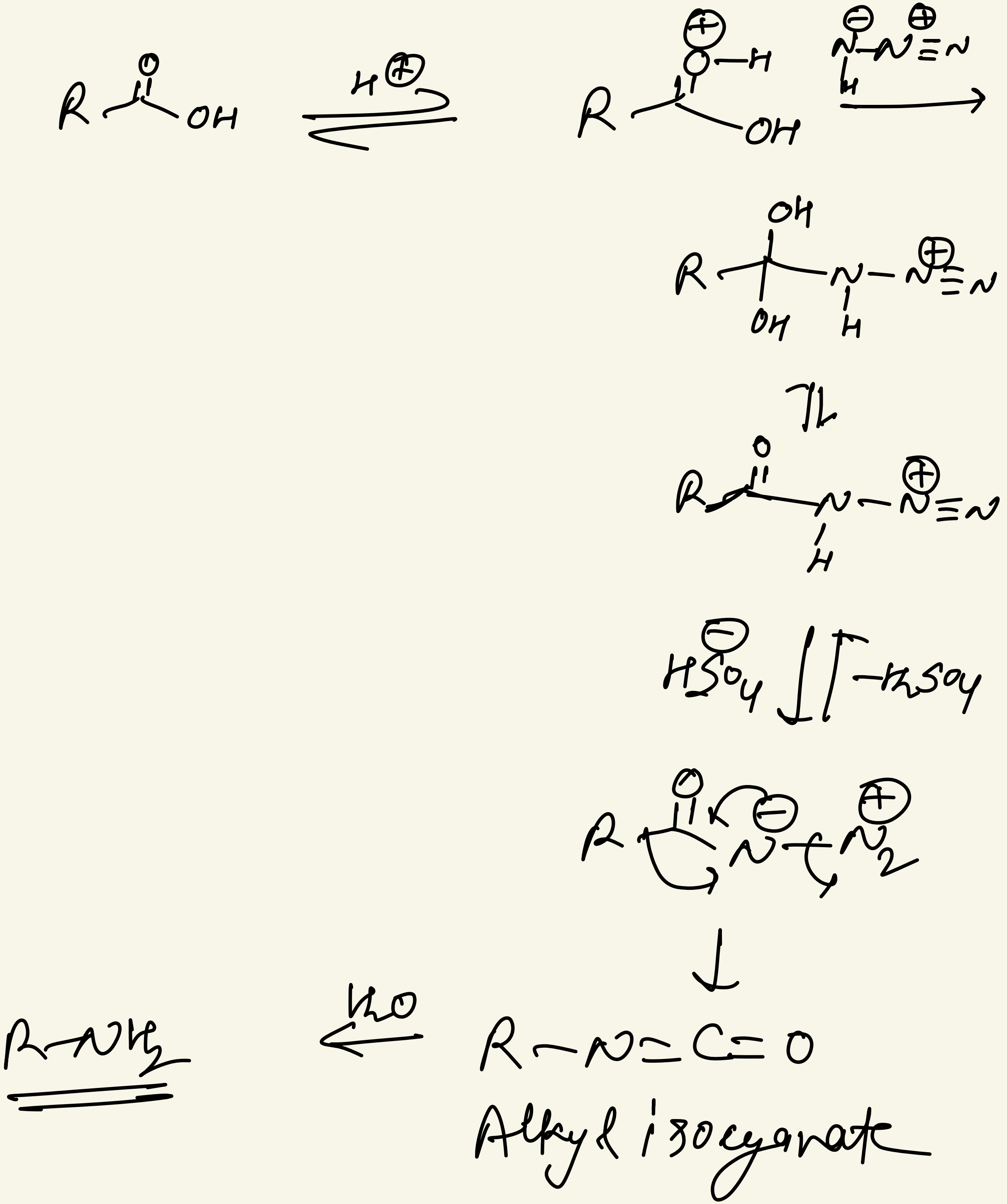
c) 

d) 

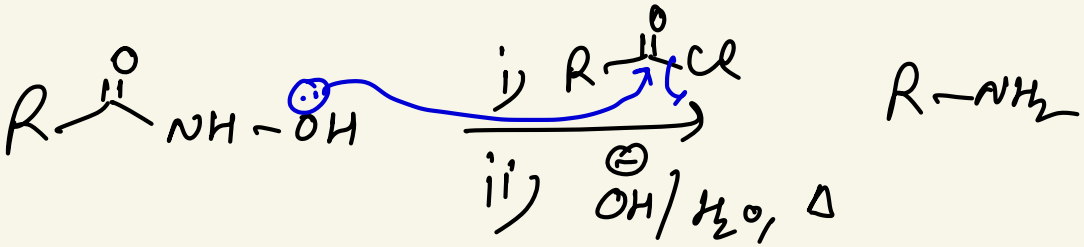
(2) Curtius Reaction :-

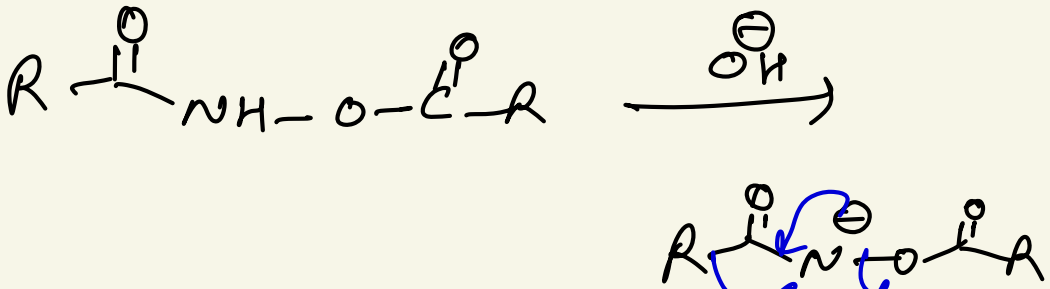


(3) Schimdt Reaction :-


H^+
H_2SO_4
$-H_2SO_4$
H_2O
R–N=C=O
Alkyl isocyanate
$R-NH_2$

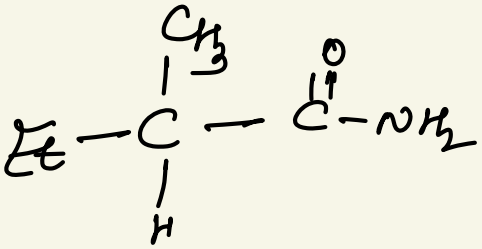
④ Lossen Rearrangement:-

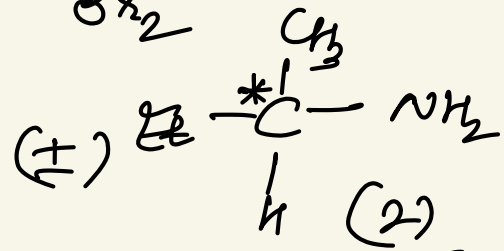




$H_2C-N=C=O$ → Bhopal gas tragedy.
methylisocyanate

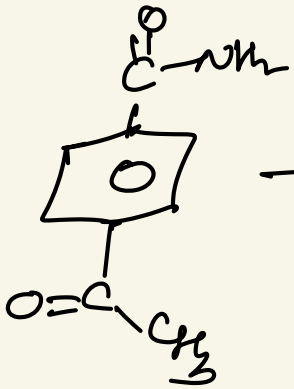
Q.



(±) 

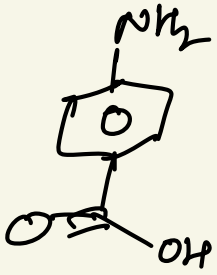
(2)

Q

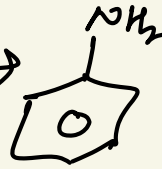


KOBr2 → X

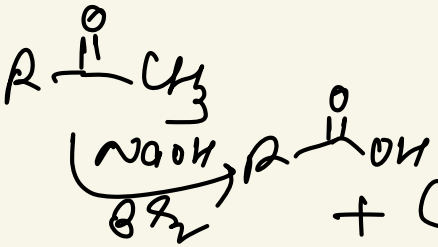
NaOH + CaO, Δ → Y



$-CO_2$

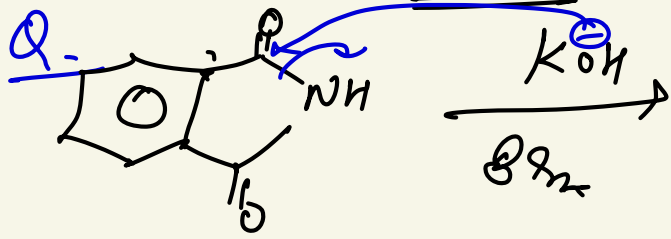


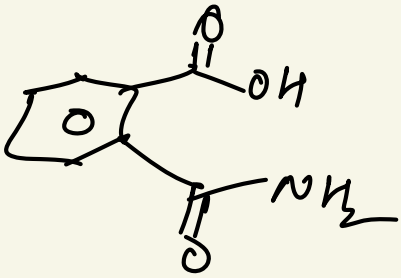
aniline



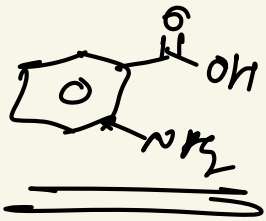
+ $CHBr_3$ ↓

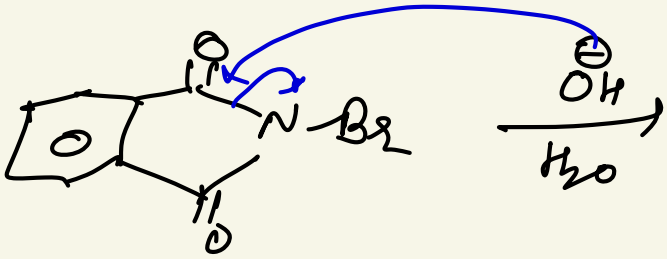
Q.

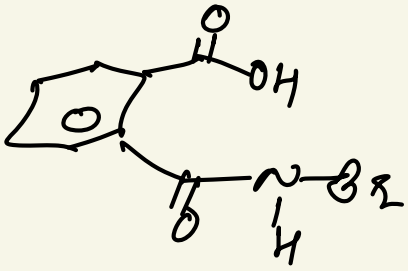


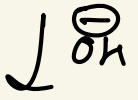


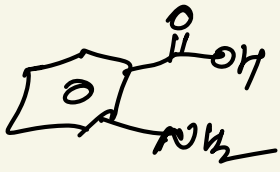
↓ KOH + Br_2



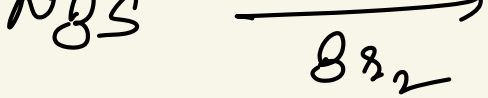


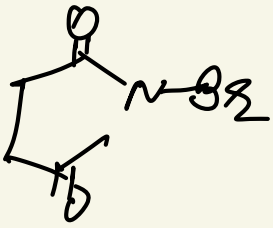


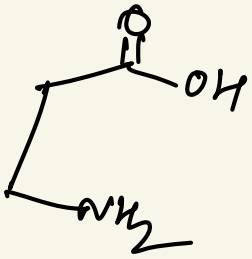




Q.







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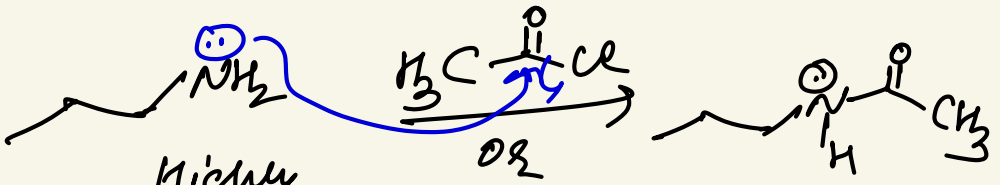
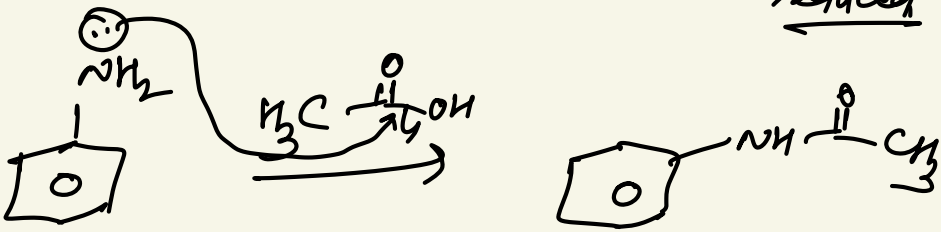


Highly basic

Basicity of N is reduced

Q.



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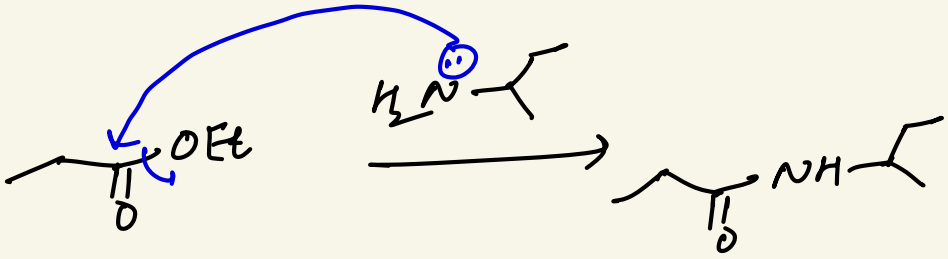

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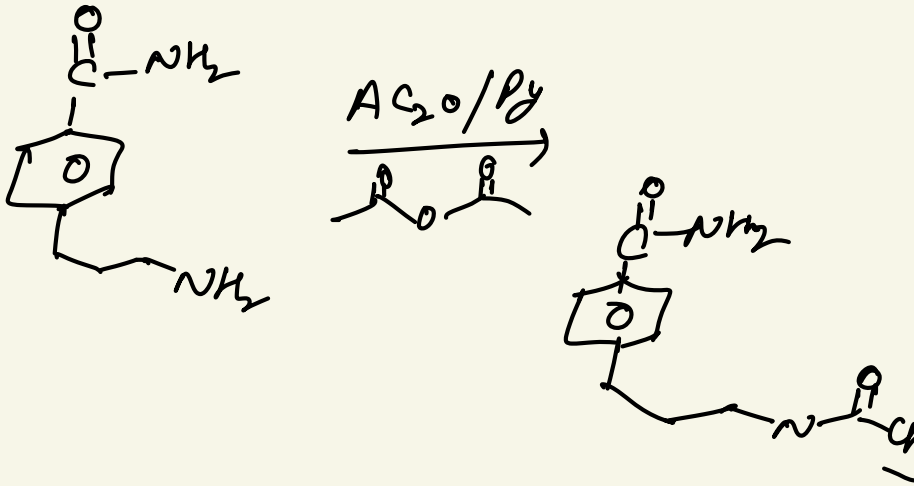
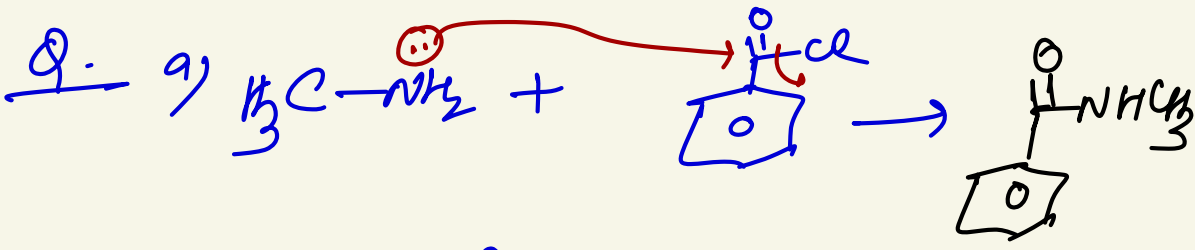
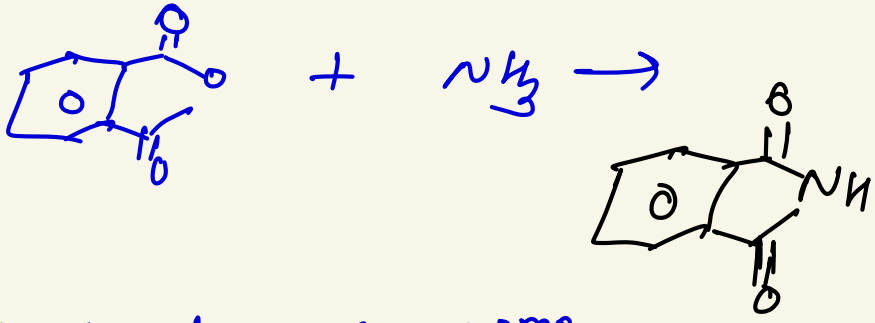
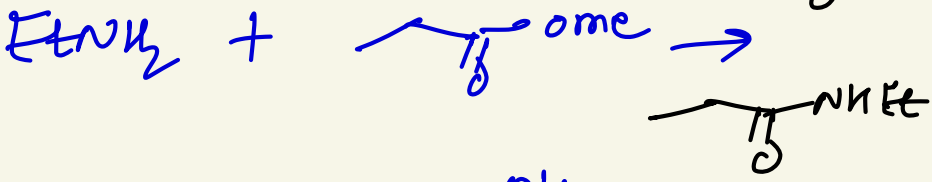
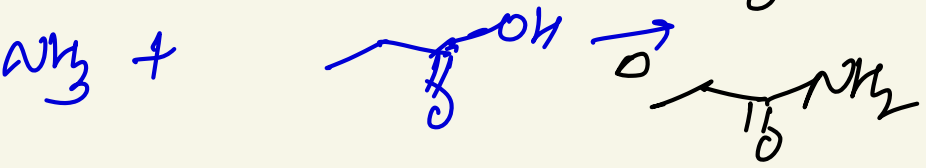
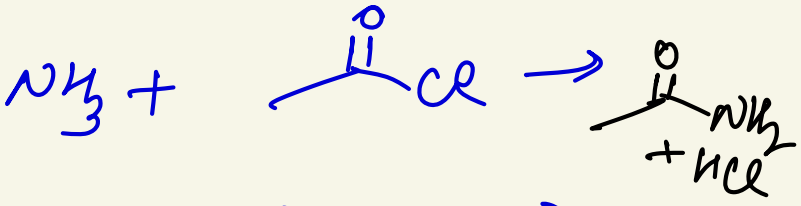


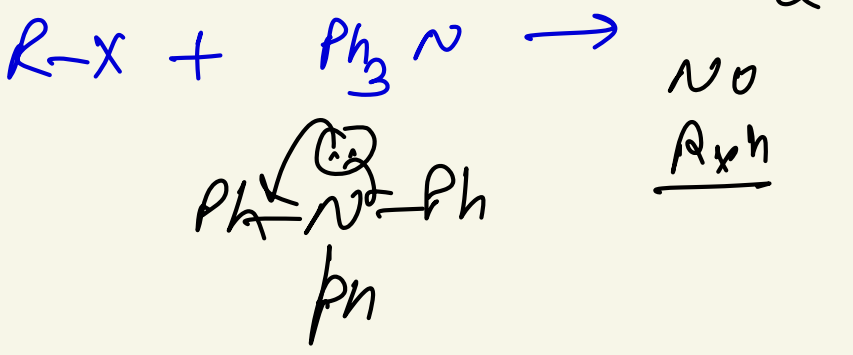
Q. a) 

b) 

c) 

d) 

e) 

f) 

Some prop. of Amine :-

Basic strength :-

(Gas phase)

Et_3N Et_2NH $EtNH_2$ NH_3

a b c d

$a > b > c > d$

In aq. phase :-

1) CH_3NH_2 $(CH_3)_2NH$ $(CH_3)_3N$ NH_3

1 2 3 4

$2 > 1 > 3 > 4$

2) $EtNH_2$ $(Et)_2NH$ $(Et)_3N$ NH_3

1 2 3 4

$2 > 3 > 1 > 4$

Detection of Amines:-

① **distillation:-** As B.Pt. of 1°, 2°, 3° amines are quite different so they can be seperated by distillation/ fractional distillation.

② **Carbylamine Reaction:-**

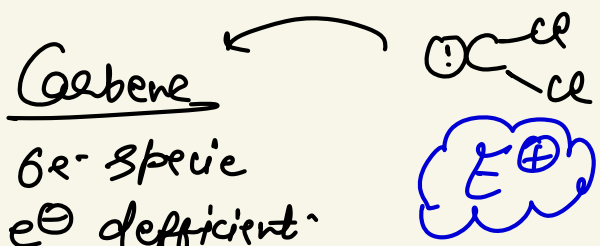
for aliphatic/aromatic 1° amine

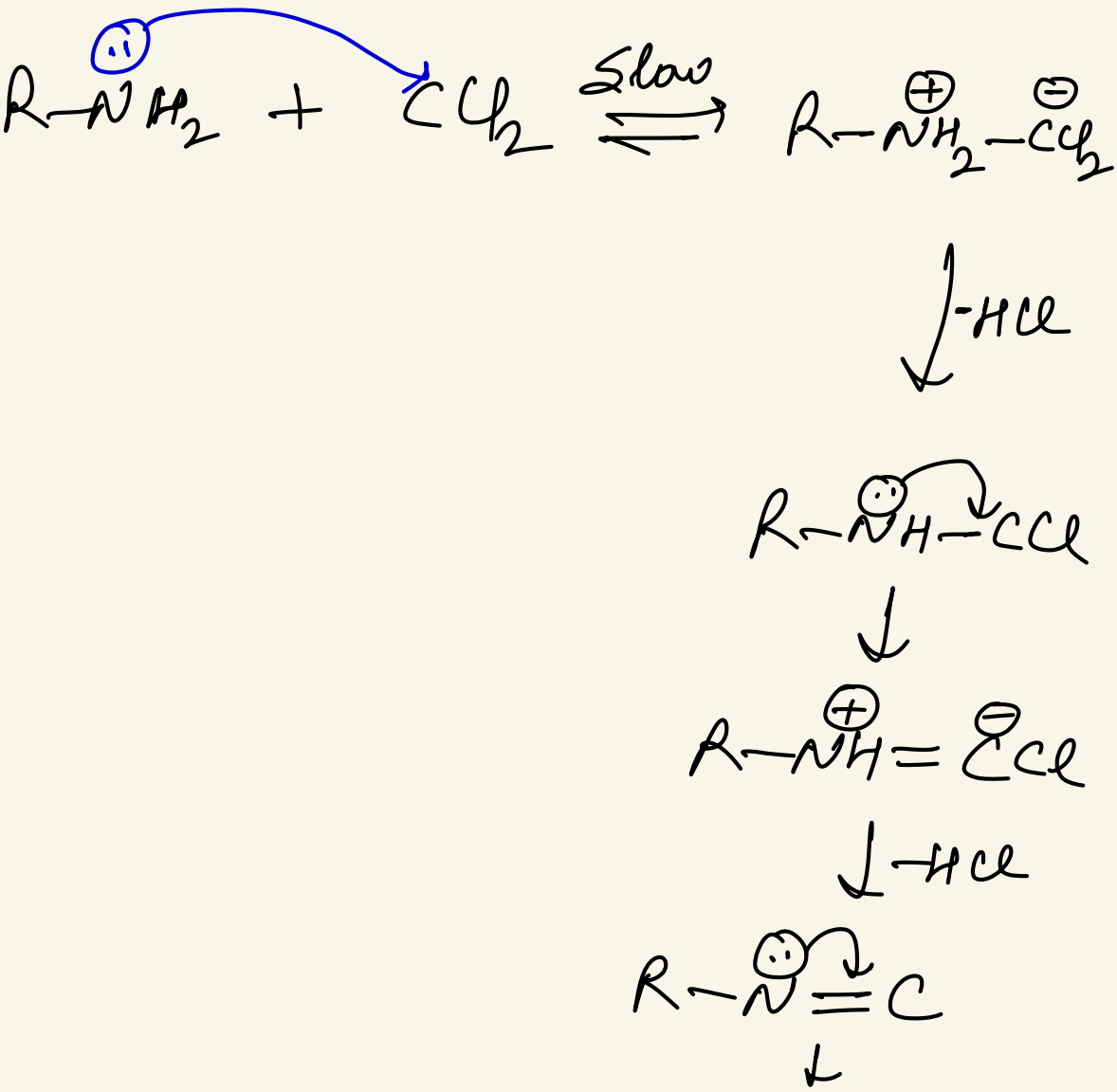
$$R-NH_2 \xrightarrow[KOH]{CHCl_3} R-\overset{\oplus}{N}\equiv\overset{\ominus}{C}$$ (Isocyanide)

foul smell

Mechanism:-

$$H-C(Cl)(Cl)(Cl) + KOH \xrightarrow{-H_2O} \overset{\ominus}{C}(Cl)(Cl)(Cl) + K^{\oplus}$$


Carbene
6e- specie
e⊖ deffficient.
E⊕

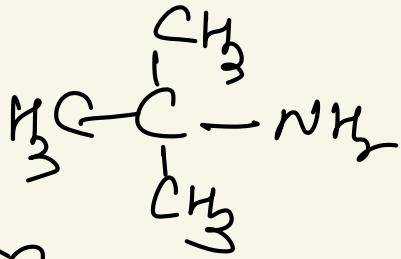

R—NH2 + CCl2
Slow
R—NH2—CCl2
-HCl
R—NH—CCl
R—NH=CCl
-HCl
R—N=C

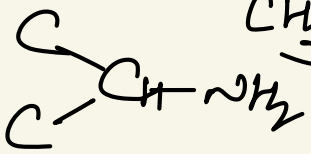
$R-N\equiv C \equiv R-\overset{\oplus}{N}\equiv \overset{\ominus}{C}$

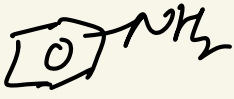
Alkyl isocyanide

2° and 3° amines doesn't give this test.

Q. How many of the following give +ve Carbylamine test?

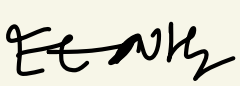
a) Tertiary butylamine 

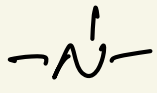
b) Isopropylamine 

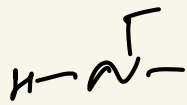
c) Aniline 

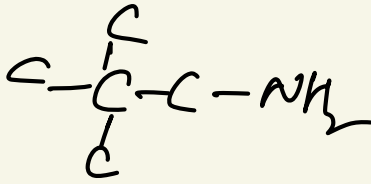
d) ✗ 

e)  1° amine

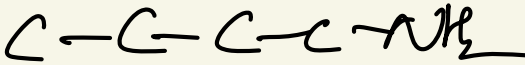
f) Ethyl amine 

g) ✗ Trimethyl amine 

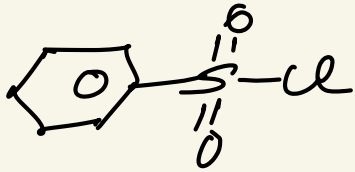
h) ✗ methyl ethyl amine 

i) ✓ Neopentyl amine 

j) ✗ n-butyl amine

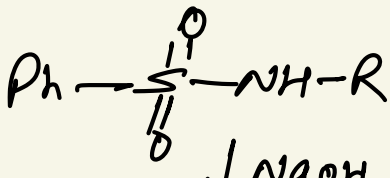
(7) 

(3) * Hinsberg test :-

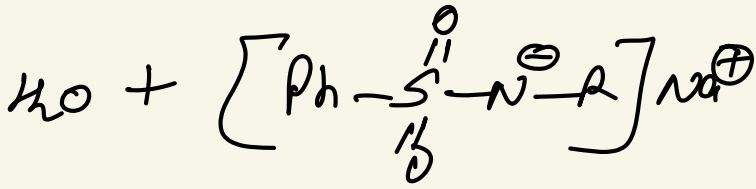
Hinsberg Regent 

($PhSO_2Cl$)

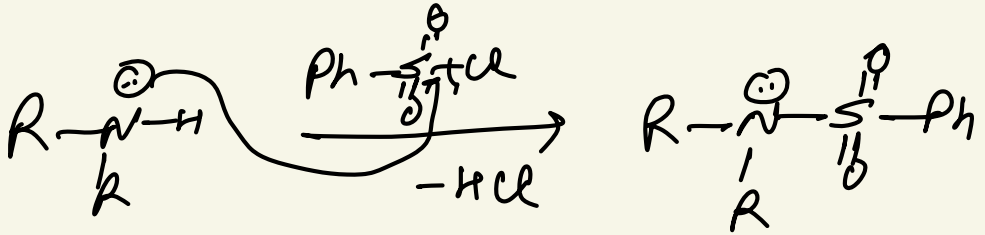
Benzene Sulphonyl Chloride

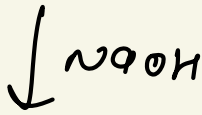
i) $R-NH_2$  

↓ NaOH

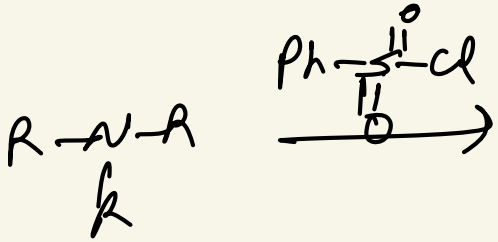


Water soluble

ii) 



Water insoluble

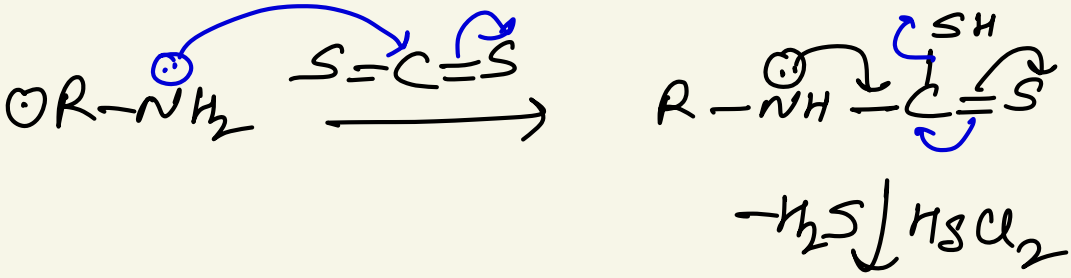
iii) 

No Rxn

1°, 2° and 3° amine can be differenciated by Hinsberg test

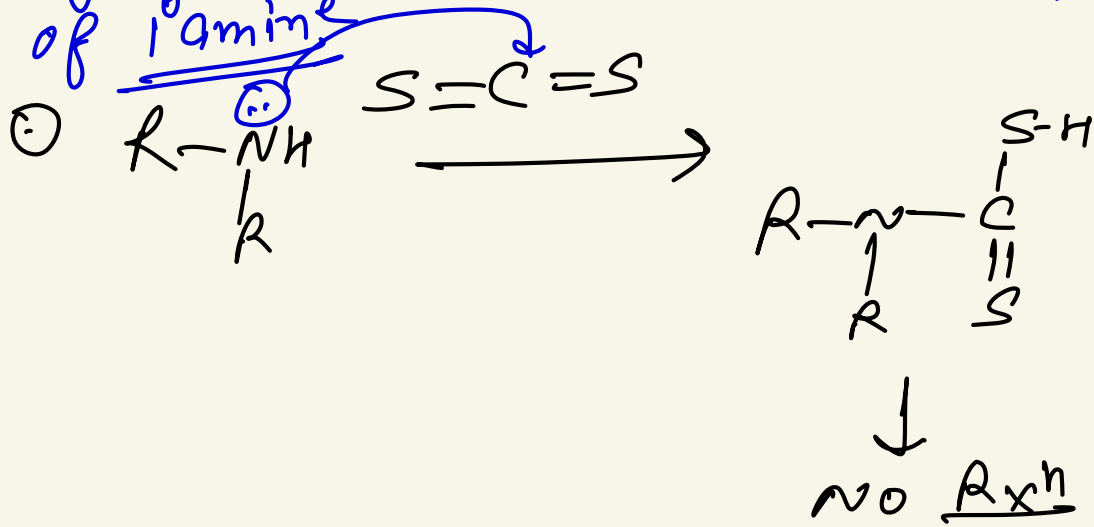
(4) Hoffmann mustard oil test :-

Regent → CS_2, $HgCl_2$



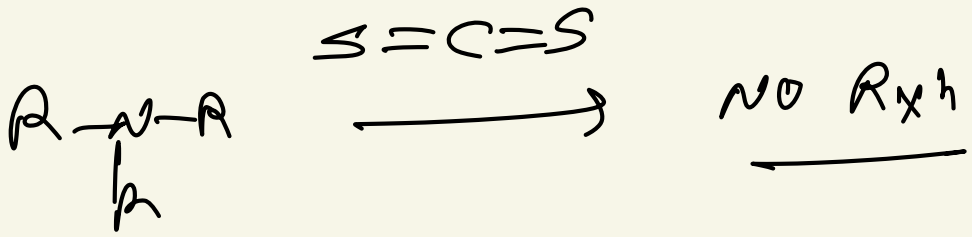
HgS (black ppt.) + $R-N=C=S$ (alkyl isothiocyanate — mustard oil smell)

Only in case of 1° amine



↓

NO Rxn

(i) 

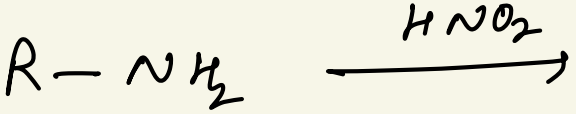
(5) Diazotisation :-

Reaction with $NaNO_2 + HCl$

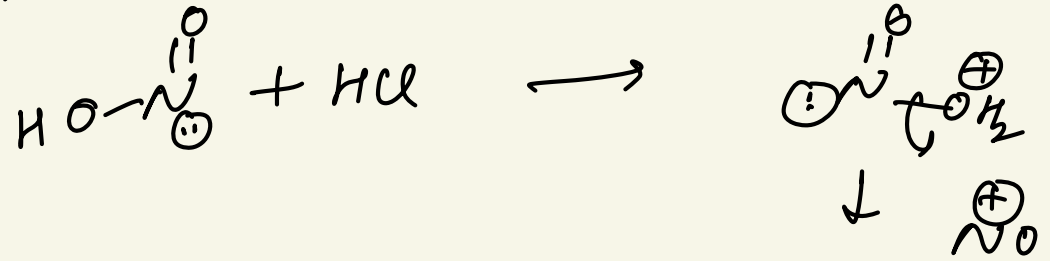
HNO_2

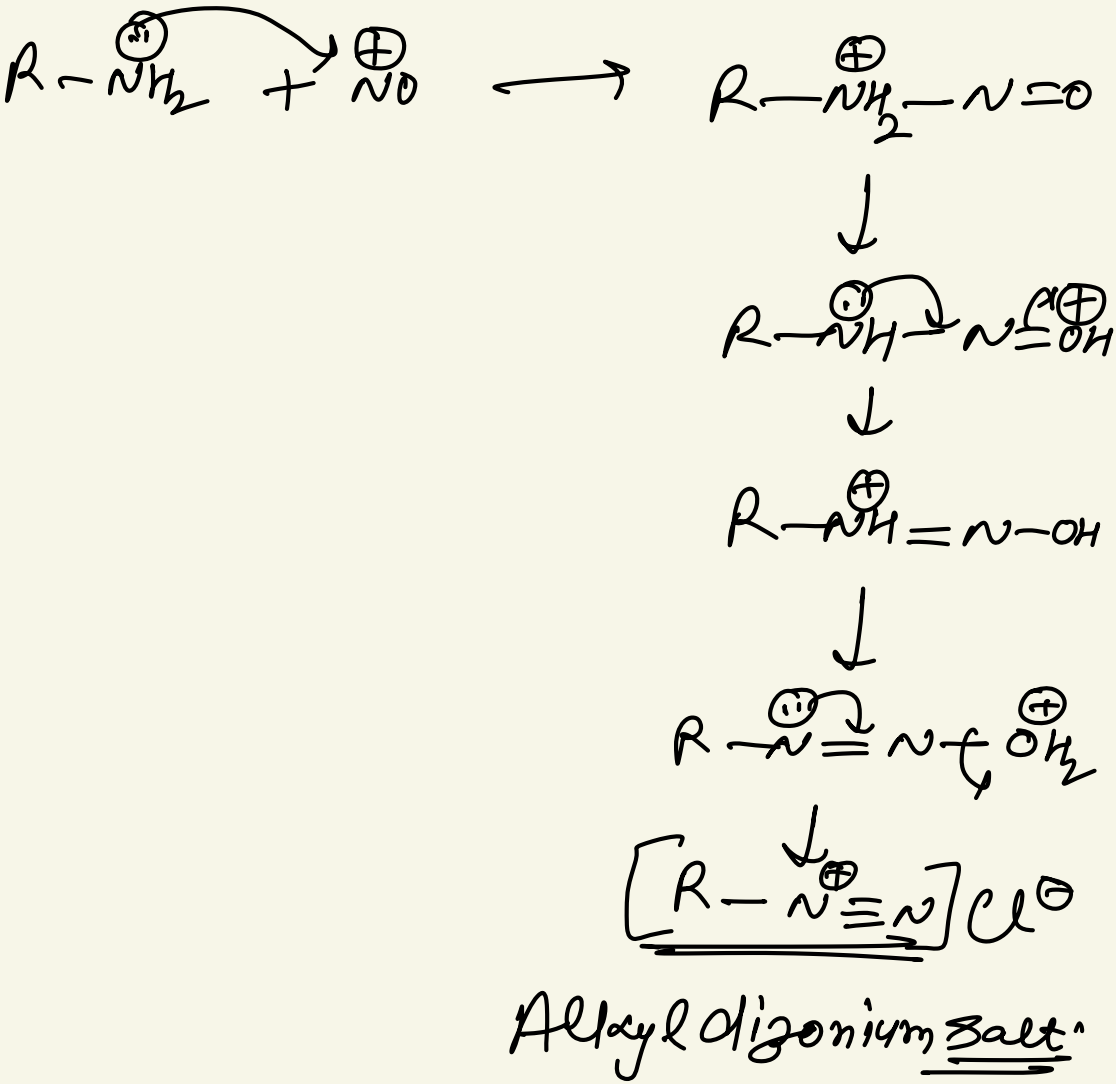
Nitrous acid.

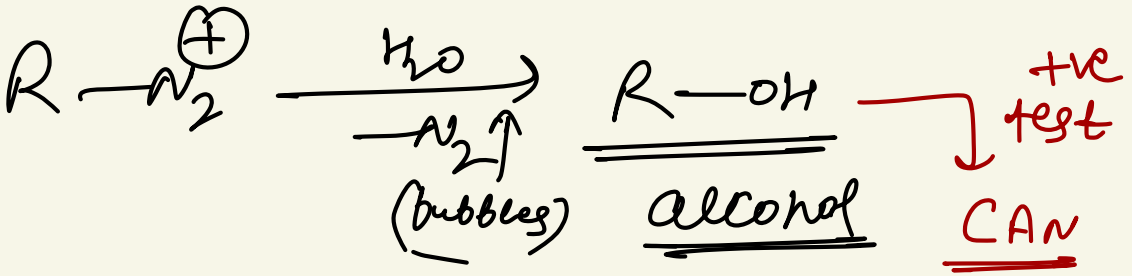
1° amine



i) Gen. of $E^{\oplus}$



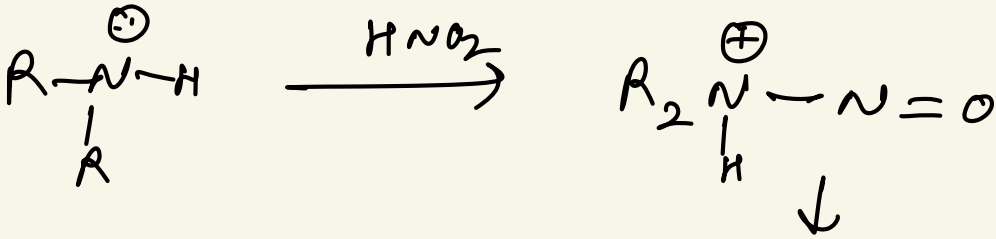




alcohol give red color with

CAN:

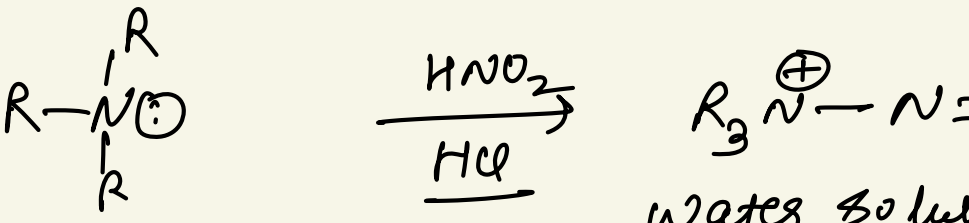
2° amine:



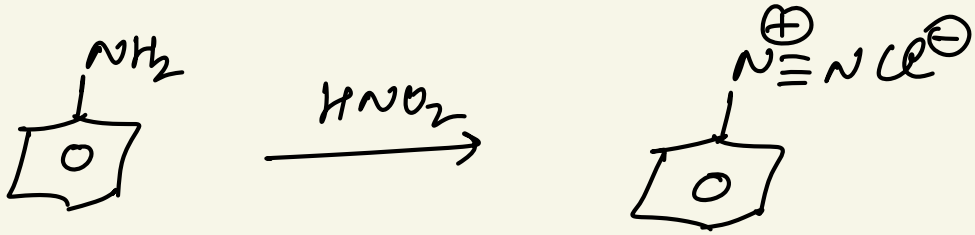
$$R_2N-N=O + H^{\oplus}$$

yellow oily layer indicates 2° amine is present

3° amine



water soluble ion pair



Benzene diazonium salt

85040830

H.W. O-I, O-II, JM Complete.