Study Material: 1

Name- Sayanwita Panja

Discipline- B.Sc (H)

Subject- Chemistry

Semester- IV

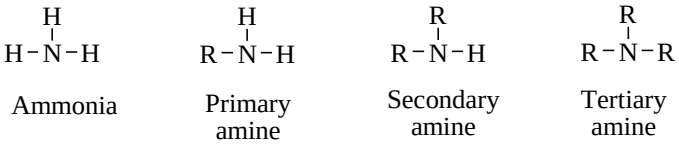
Course Code- CC10

Topic- Organic Chemistry, Nitrogen Compounds

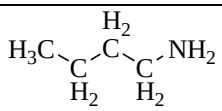
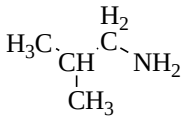
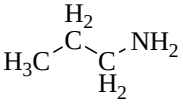
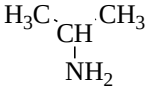
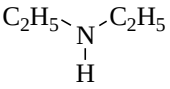
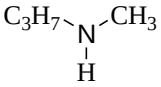
ORGANIC COMPOUNDS OF NITROGENS:

Aliphatic Amines:

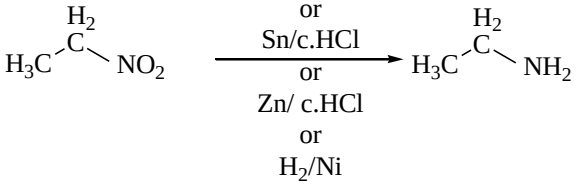
Amines may be regarded as derivatives of ammonia, in which one or more hydrogen atoms have been replaced by alkyl groups.

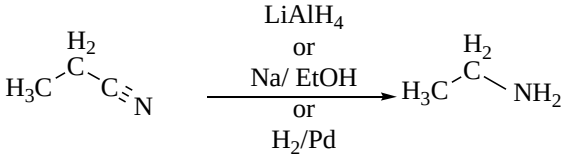


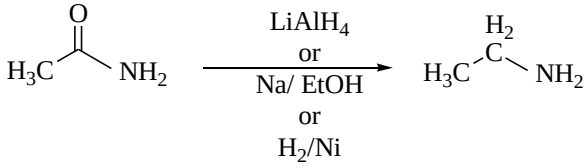
- **Isomerism:**

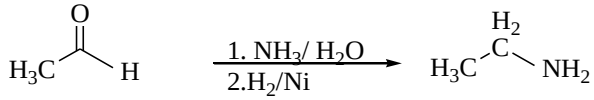
Chain Isomerism	Position Isomerism	Functional Isomerism	Metamerism
 n-Butylamine  Isobutylamine	 1-Aminopropane  2-Aminopropane	$CH_3.CH_2.CH_2.NH_2$ Propylamine (Primary) $CH_3.NH.C_2H_5$ Methylethylamine (Secondary) $(CH_3)_3N$ Triethylamine (Tertiary)	 Diethylamine  Methylpropylamine

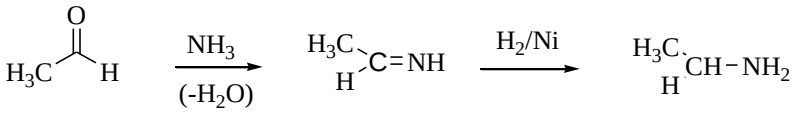
- **General methods of preparation of amines:**

1. 

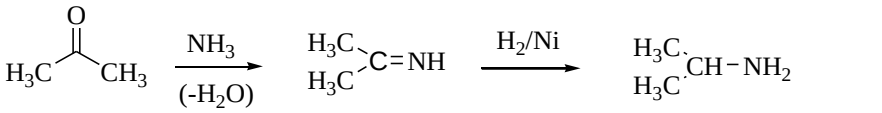
2. 

3. 

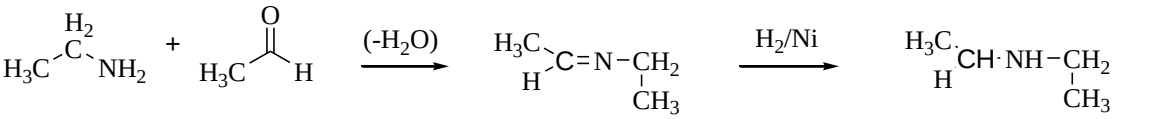
4. 



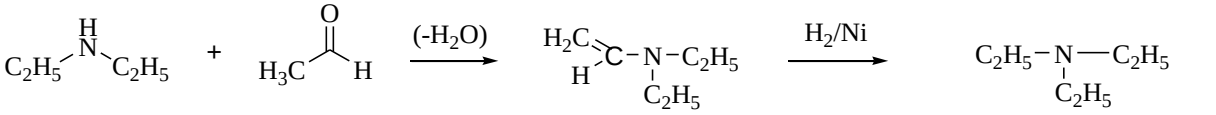
Ethylamine (1^o amine)



Isopropylamine (1^o amine)



Diethylamine (2^o amine)



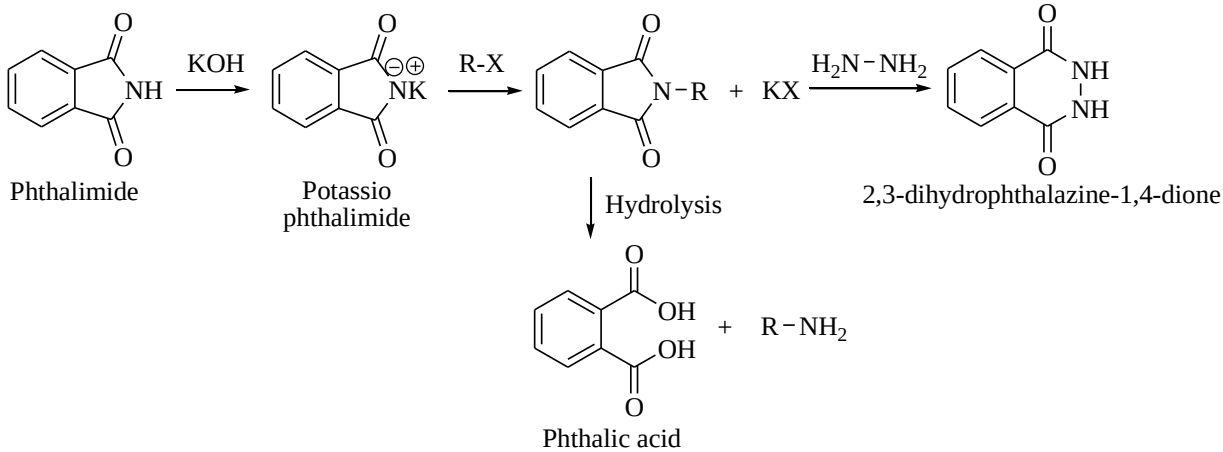
Triethylamine (3^o amine)

5. Reaction of Chloramine on Grignard reagent:

$RMgX + Cl\text{-}NH_2 \longrightarrow RNH_2 + Mg(X)Cl$

$(CH_3)_3CMgI + Cl\text{-}NH_2 \longrightarrow (CH_3)_3C\text{-}NH_2 + Mg(I)Cl$

6. Gabriel's Phthalimide Synthesis: (1^o amine synthesis)

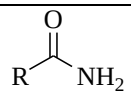
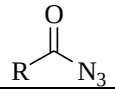
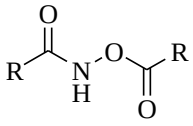
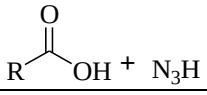


Phthalimide — Potassio phthalimide — 2,3-dihydrophthalazine-1,4-dione

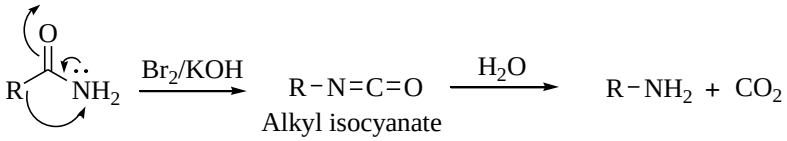
Hydrolysis

Phthalic acid

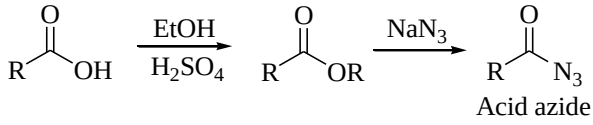
7. Hofmann, Curtious, Lossen, Schmidt Reaction: (1° amine synthesis)

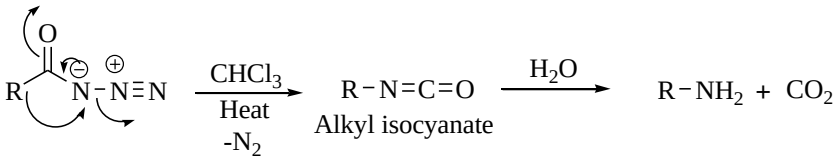
Rearrangement	Substrate	Reagent	Intermediate	Product
Hofmann		Br_2/KOH	R-N=C=O	R-NH_2
Curtious		Heating in $CHCl_3$	R-N=C=O	R-NH_2
Lossen		C_2H_5ONa	R-N=C=O	R-NH_2
Schmidt		H_2SO_4	R-N=C=O	R-NH_2

i. Hofmann Reaction:

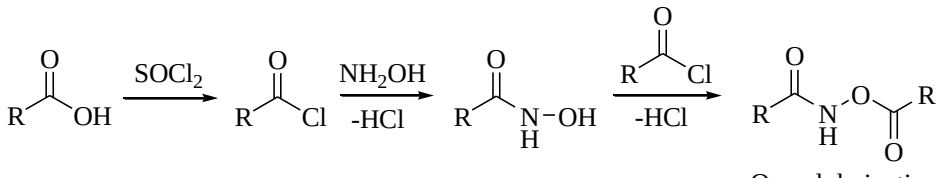


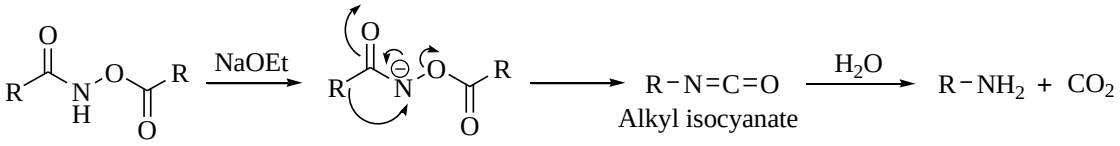
ii. Curtious Reaction:



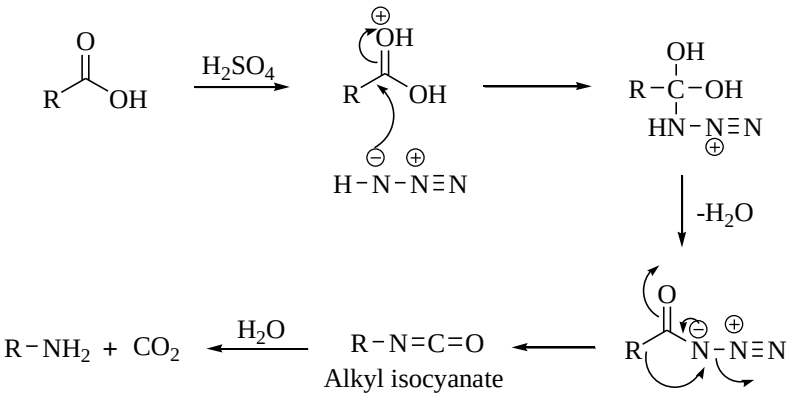


iii. Lossen Reaction:

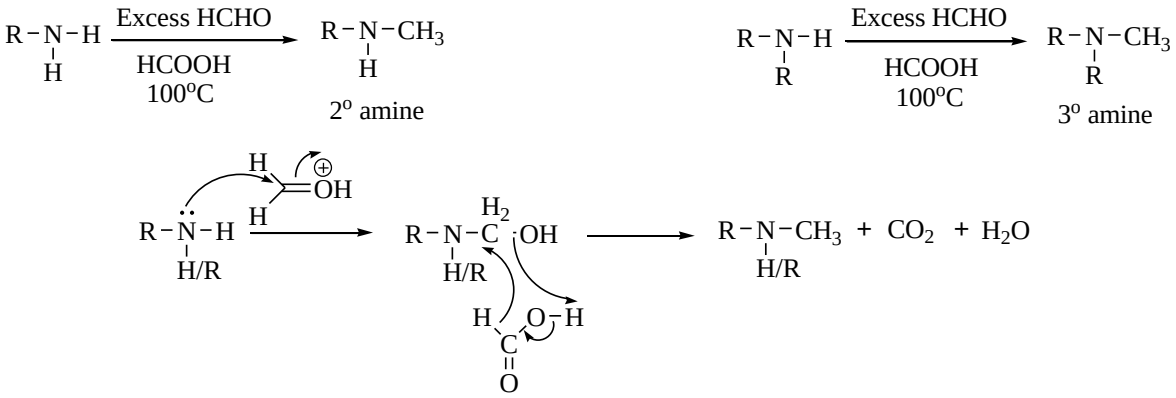




iv. Schmidt Reaction:



8. Eschwieler Clarke Methylation: (E-Clarke Reaction, 2º or 3º amine synthesis)



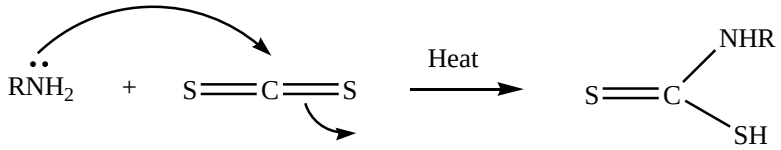
- **Reaction of Primary Amine:**

1. Carbylamine Reaction:

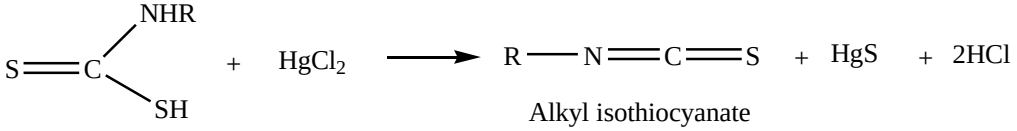
$$C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$$

Ethyl isocyanide

2. Hofmann's Mustard Oil Reaction:



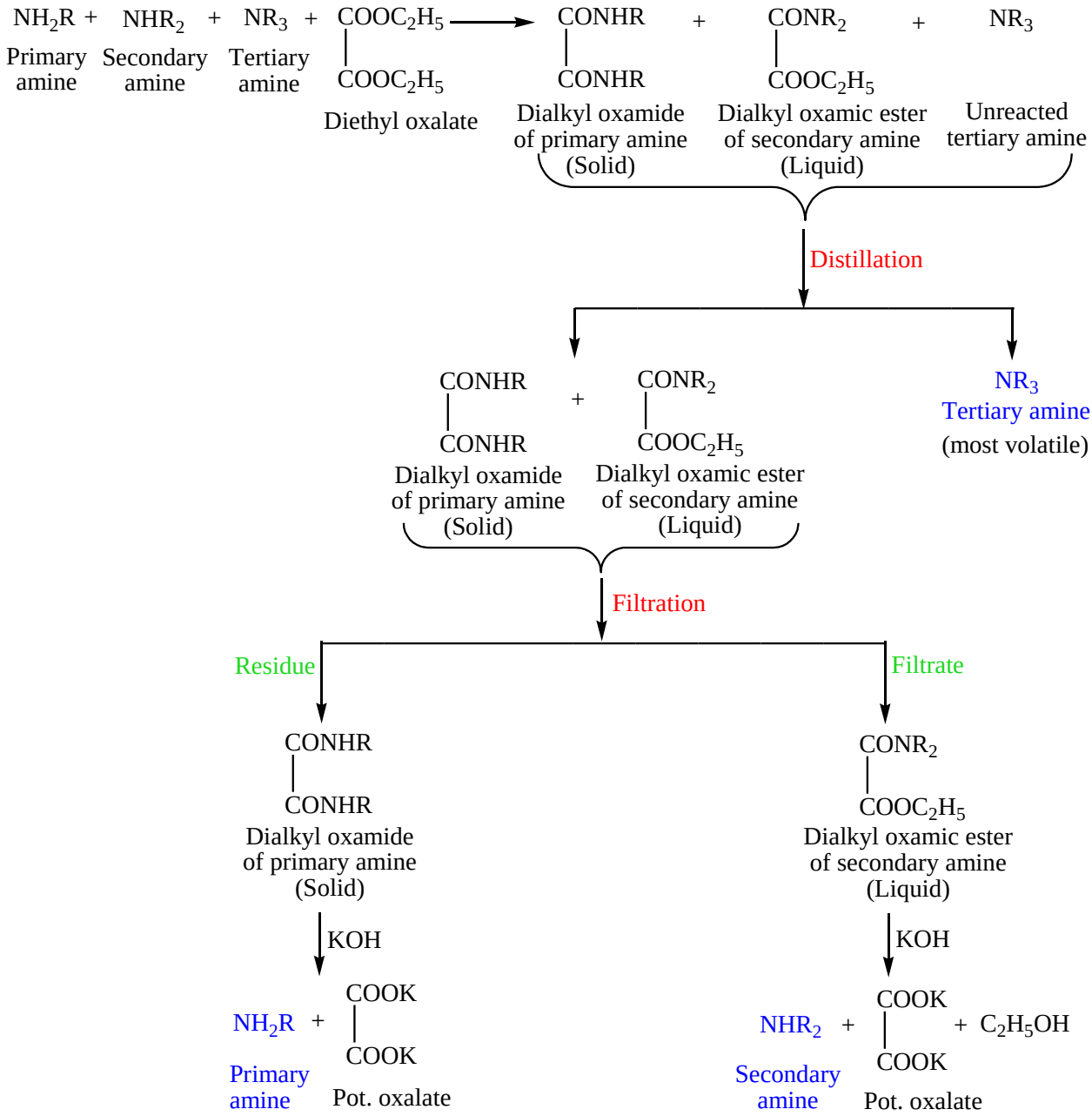
Monoalkyl-dithiocarbamic acid



Alkyl isothiocyanate
(smell of mustard oil)

- **Separation of mixture of Amines:**

1. **Hofmann Method:**



2. Hinsberg Method: