

# Important Question

1.

12/10/2020 (From Previous Year) By-Dr.Rinky

## For Degree-I (Hons.)

### Question

a. Give a brief account of primary, secondary & tertiary amines.

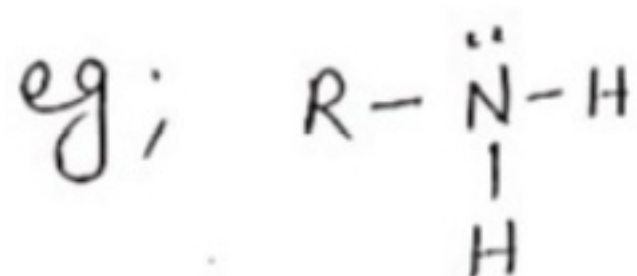
b. Compare basic strength of  $1^\circ$ ,  $2^\circ$  &  $3^\circ$  amines.

### Answer

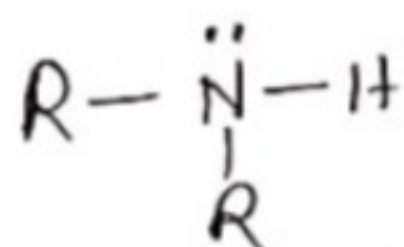
a. Brief account of  $1^\circ$ ,  $2^\circ$  &  $3^\circ$  amines :-

\* Amines are classified as Primary ( $1^\circ$ ), secondary ( $2^\circ$ ) or Tertiary ( $3^\circ$ ) according to the number of alkyl groups attached to the nitrogen atom.

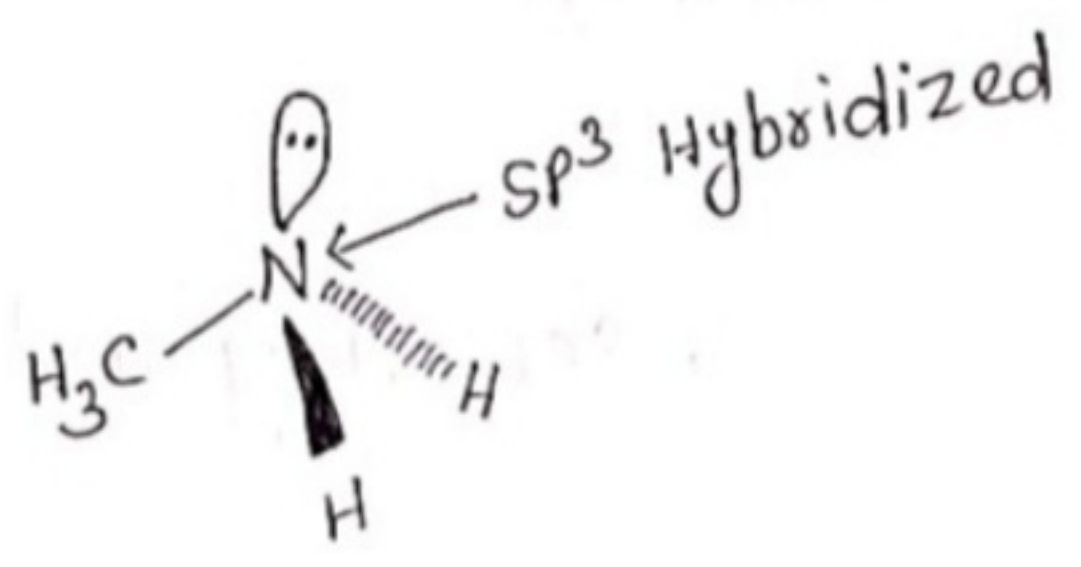
\* **Primary amine** :- It has only one alkyl group directly attached to the nitrogen.



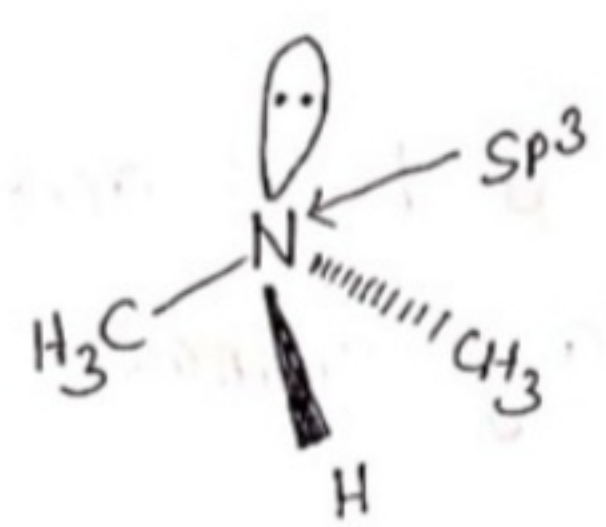
\* **Secondary amine** :- It has two alkyl groups directly attached to the nitrogen.



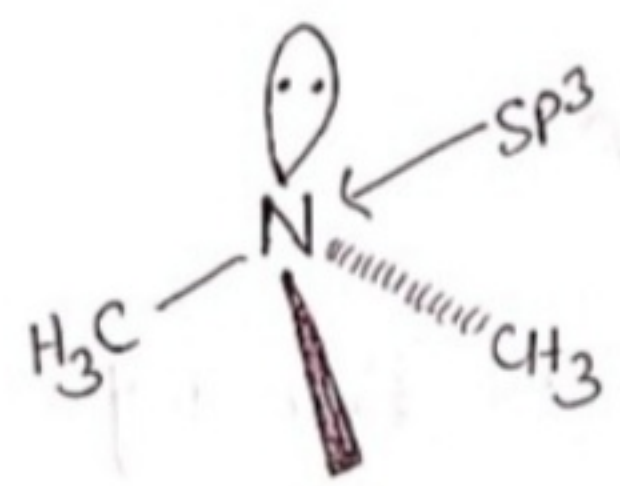
\* **Tertiary amine** :- A tertiary amine has three alkyl groups directly attached to the nitrogen.



**Methyl amine**  
(1°)



**Dimethyl amine**  
(2°)



**Trimethyl amine**  
(3°)

**Ans.**

## b. BASIC STRENGTH OF AMINE

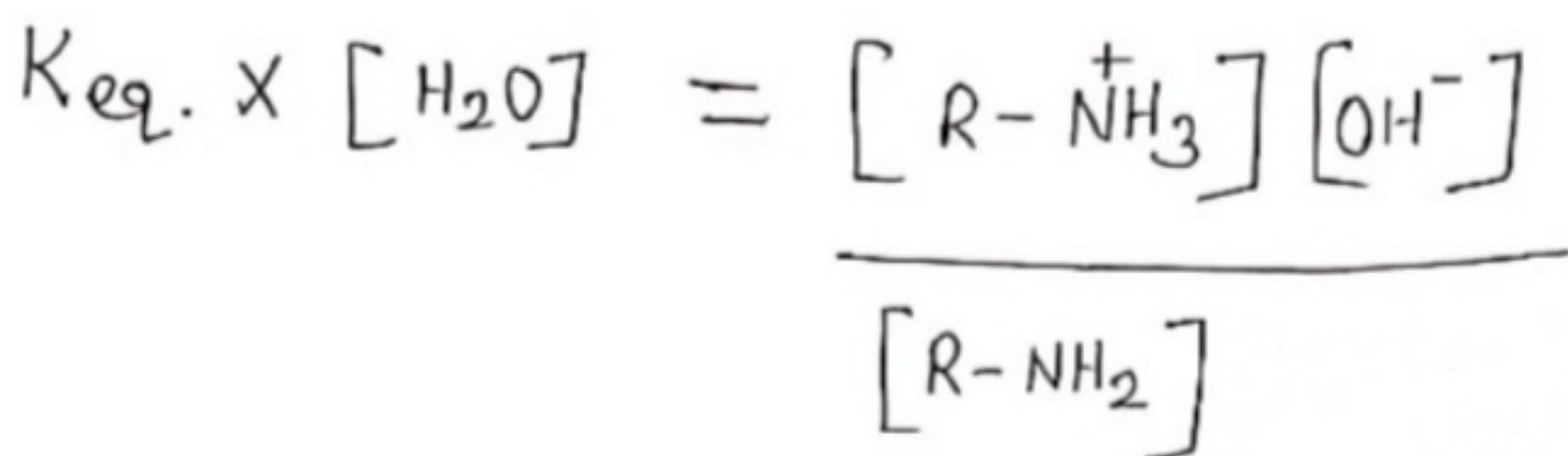
\* Due to presence of lone pair of electron, amines are Lewis base.



$$K_{eq} = \frac{[R-\overset{\oplus}{N}H_3][OH^-]}{[R-NH_2][H_2O]}$$



$\therefore [H_2O]$  is large excess, hence taken as const.



$$\therefore K_b = \frac{[R-NH_3^+][OH^-]}{[R-NH_2]}$$

Where,  $K_b$  = Dissociation const. of base.

$$** \quad \boxed{\text{Basic strength} \propto K_b}$$

As  $K_b$  increases, basic strength of amine increases.

$$\therefore pK_b = -\log K_b$$

$$\therefore pK_b = \log \frac{1}{K_b}$$

$$\therefore \boxed{pK_b \propto \frac{1}{K_b}}$$

$$\therefore \boxed{pK_b \propto \frac{1}{K_b} \propto \frac{1}{\text{Basic strength}}}$$

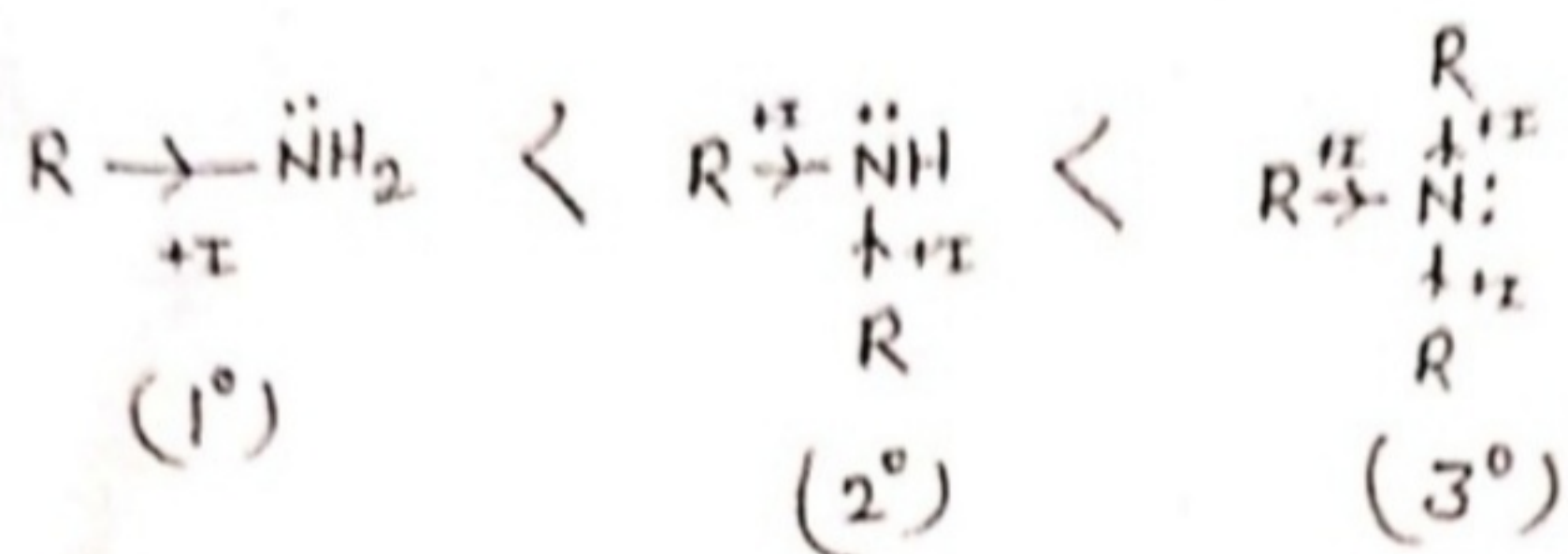
\* Basic strength of amine is inversely proportional to  $pK_b$ .

ie; Higher the  $pK_b$  value of amine, lesser will be their basic strength.

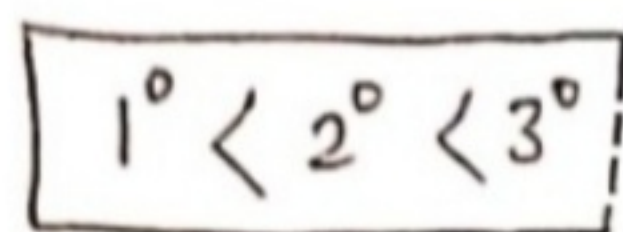
# BASIC STRENGTH OF 1°, 2° & 3° AMINE

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## In Gaseous Phase



\* With increase in no. of alkyl group attached to nitrogen, the electron density increases hence, the basic strength is in following order.

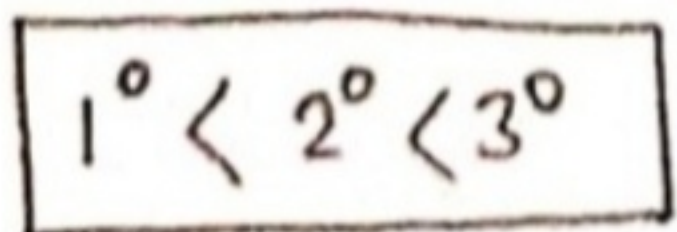


## In Aqueous Solution

The basic strength of amine is subtle interplay of the following three effect:-

1. Inductive effect
2. Solvation effect
3. Steric effect.

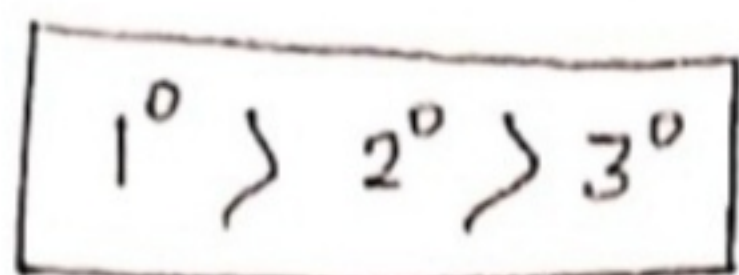
\* On the basis of inductive effect; the order should be



But in aqueous solution the conjugate acid of 1° amine is more stable than that of 2° and conjugate acid of



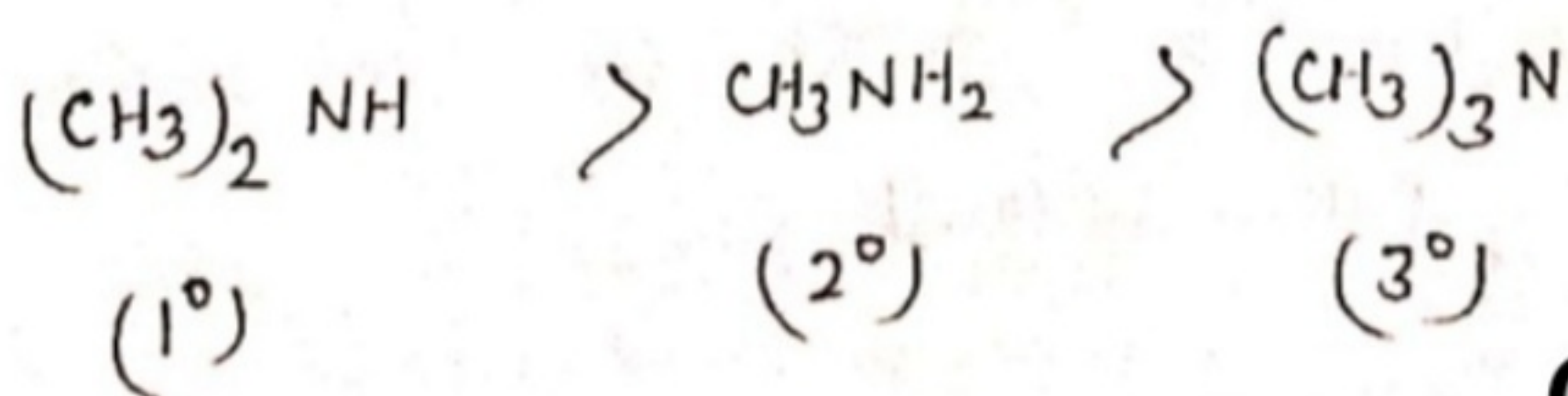
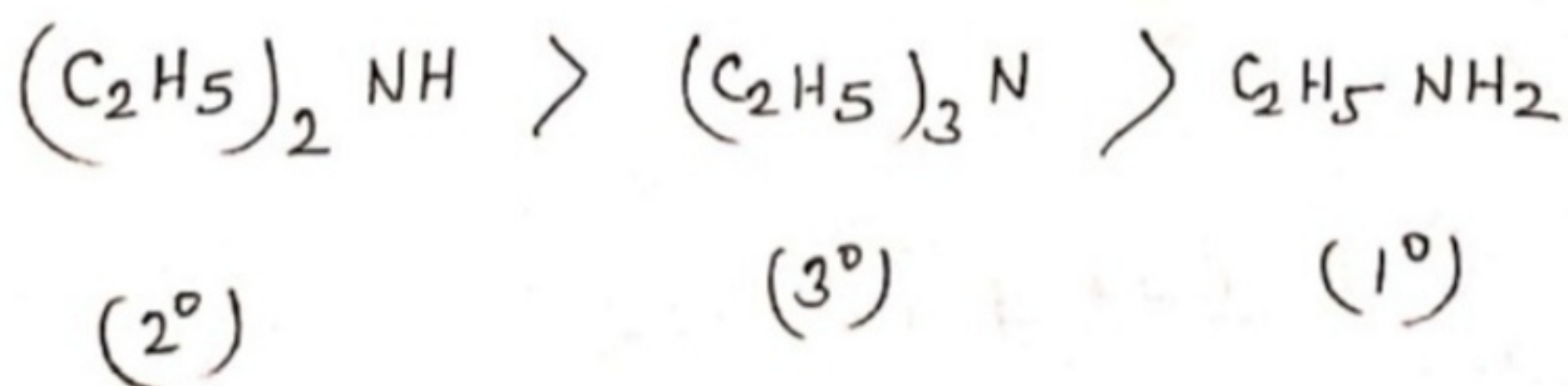
5.  
2° amine is more stable than that of 3° due to solvation effect. Therefore, Basic strength should be -



- \* Size of alkyl group decide steric effect.
- \* When the alkyl group is small like  $-\text{CH}_3$ , there is no steric effect.
- \* In case of bigger alkyl group there is steric hindrance due to H-bonding.

So, conclusively the order of basic strength is subtle interplay of these effect.

- \* The order of basic strength in case of methyl substituted amines in aqueous solution is as follows.



**Completed..**