

Important Questions

1.

(From Previous year)

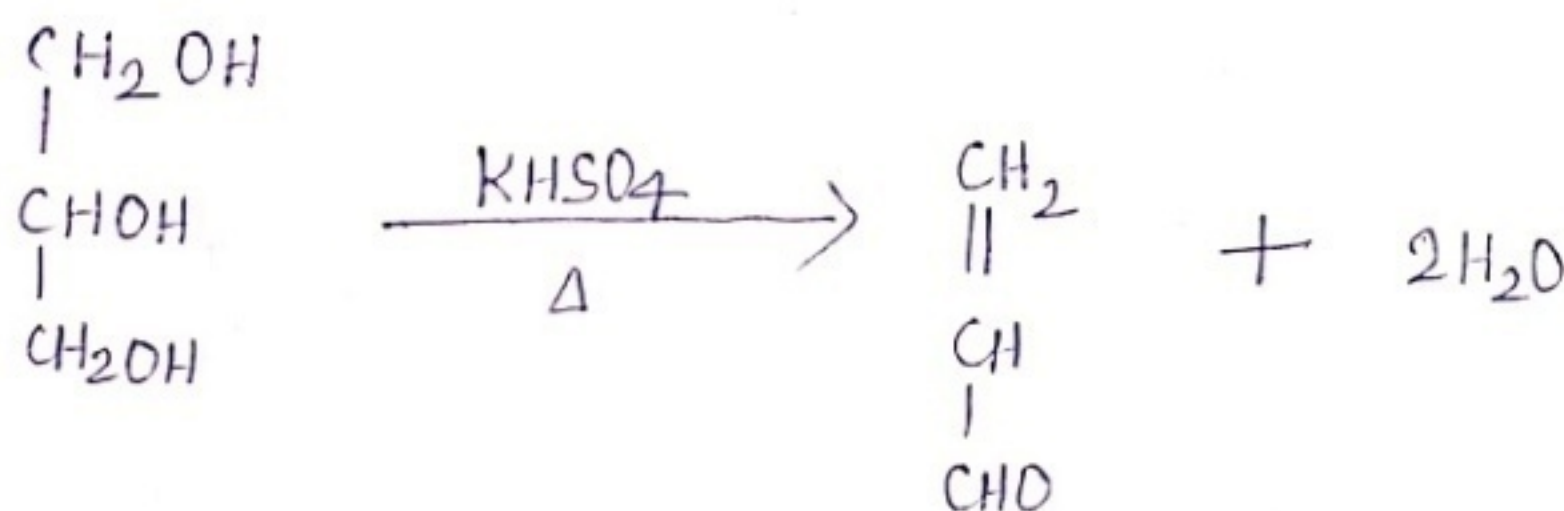
For Degree-I (Sub.)

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31-07-2020

What happens when :-

Glycerol is heated with KHSO_4

Ans. Glycerol on heating with KHSO_4 , undergoes dehydration with removal of two water molecule from the glycerol molecule. Hence, resulting in formation of unsaturated aldehyde acrolein which has a bad odour.

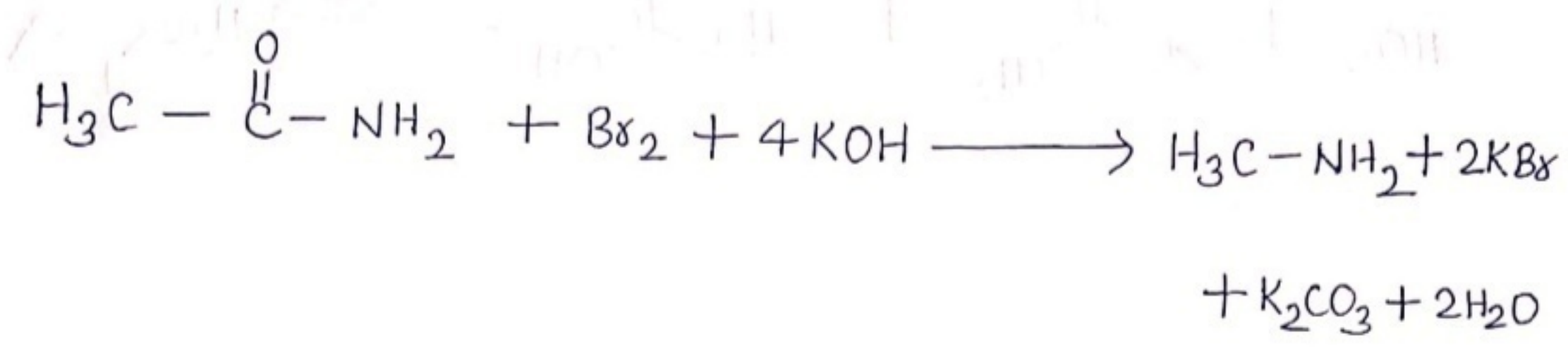


Acrolein

(Acraldehyde)

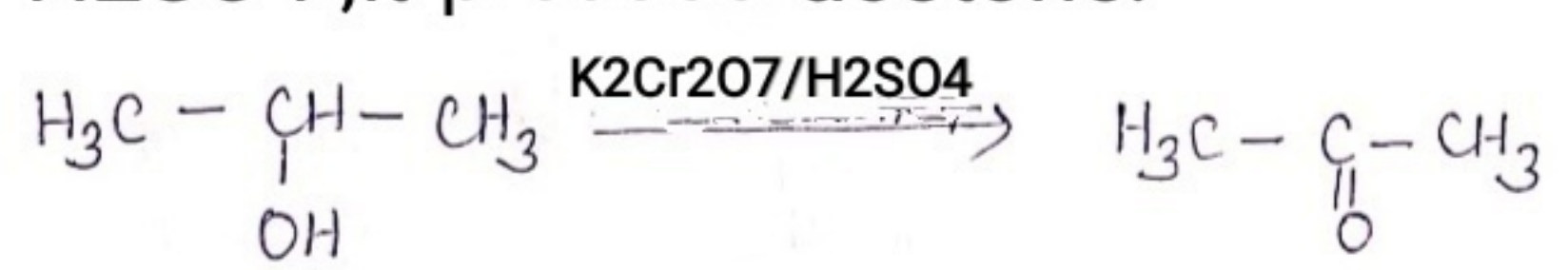
Q. Acetamide is treated with Br₂/KOH 2.

Ans. Acetamide, when treated with bromine in the presence of potassium hydroxide solution, methyl amine is formed. This reaction is known as Hofmann bromamide reaction.



Q. Isopropyl alcohol is treated with K₂Cr₂O₇/H₂SO₄

Ans. When isopropyl alcohol is treated with K₂Cr₂O₇/H₂SO₄, it produces acetone.



Isopropyl alcohol

Propanone

Q. BASIC STRENGTH OF AMINES

Ans. Due to presence of lone pair of electron, amines are Lewis Base.



$$K_{\text{eq}} = \frac{[\text{R} - \overset{+}{\text{N}}\text{H}_3] [\overset{-}{\text{O}}\text{H}]}{[\text{R} - \text{NH}_2] [\text{H}_2\text{O}]}$$

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

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

$$\therefore K_b = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

Where, K_b = dissociation const. of base.

**
* Basic strength $\propto K_b$

As K_b increases, basic strength of amine increases.

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

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

$$\therefore \text{p}K_b \propto \frac{1}{K_b}$$

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

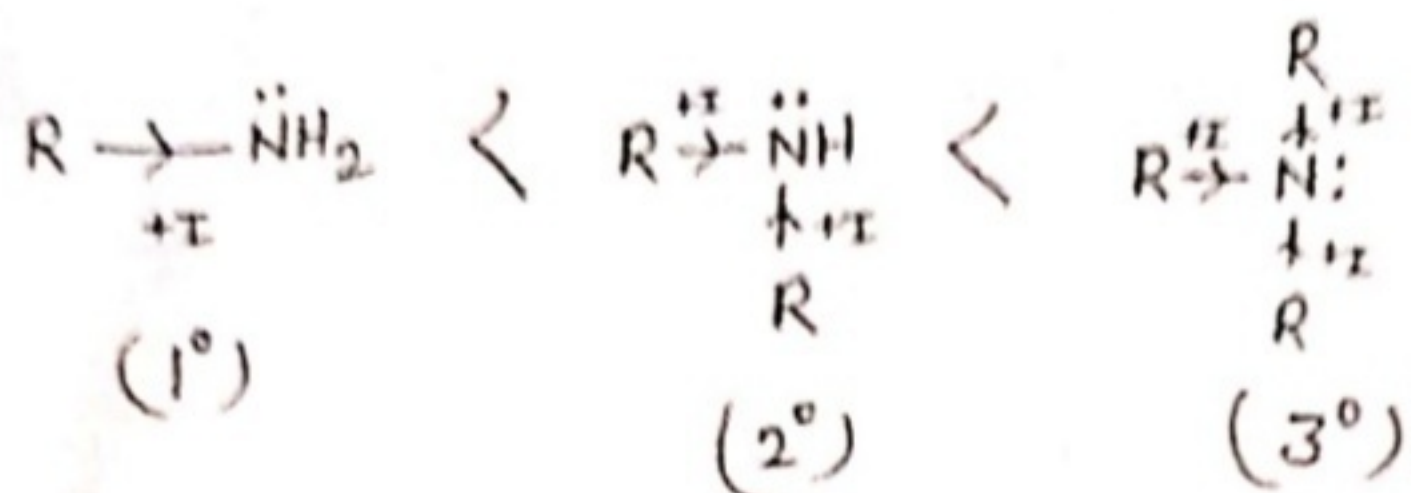
* Basic strength of amine is inversely proportional to pK_b .

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

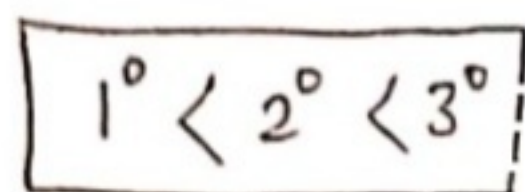
BASIC STRENGTH OF 1°, 2° & 3° AMINE

4.

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.

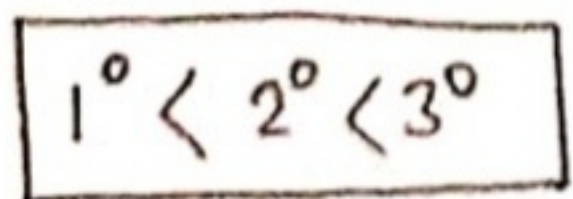


In Aqueous Solution

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

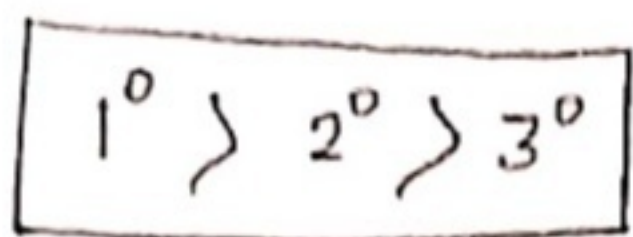
1. Inductive effect
2. Solvation effect
3. Steric effect.

* 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

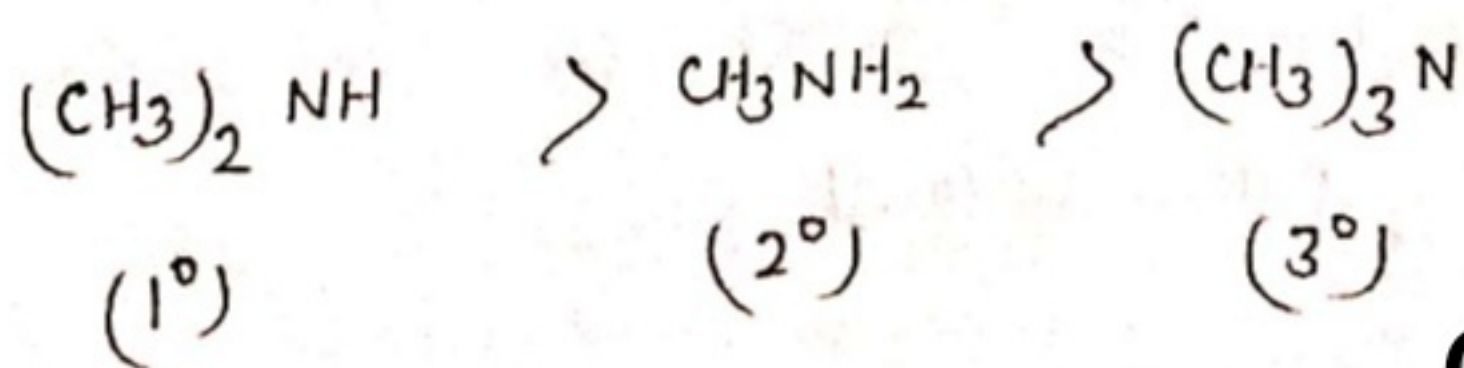
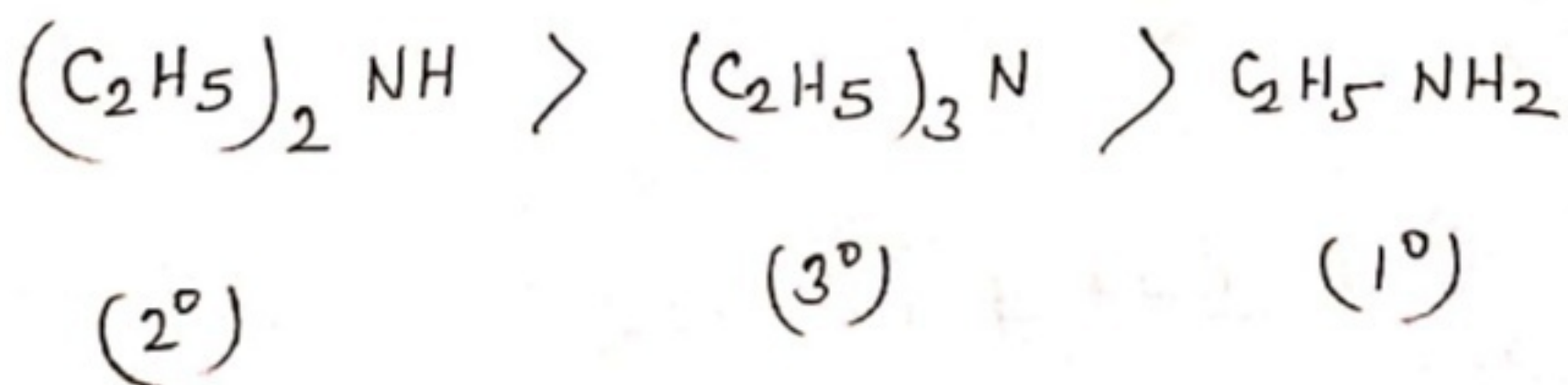
5.
2° amine is more stable than that of 3° due to solvation effect. Therefore, Basic strength should be -



- * 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..