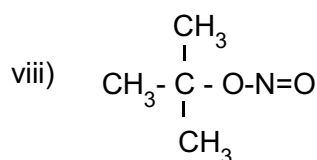
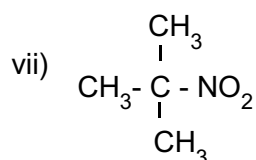
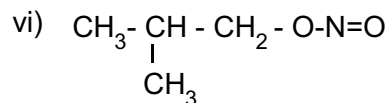
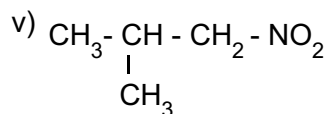
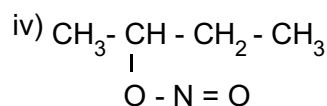
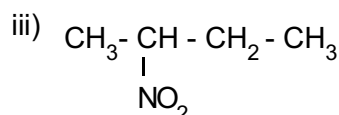
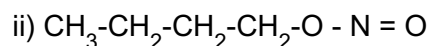
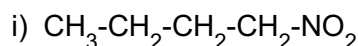


## ORGANIC NITROGEN COMPOUNDS

1. Write down the possible isomers of the  $C_4H_9NO_2$  give their IUPAC names



i) 1- nitro butane

ii) 1-nitrosooxybutane

iii) 2 - nitro butane

iv) 2- nitroso oxy butane

v) 2- methyl - 1- nitro propane

vi) 2 - methyl -1-nitroso oxy propane

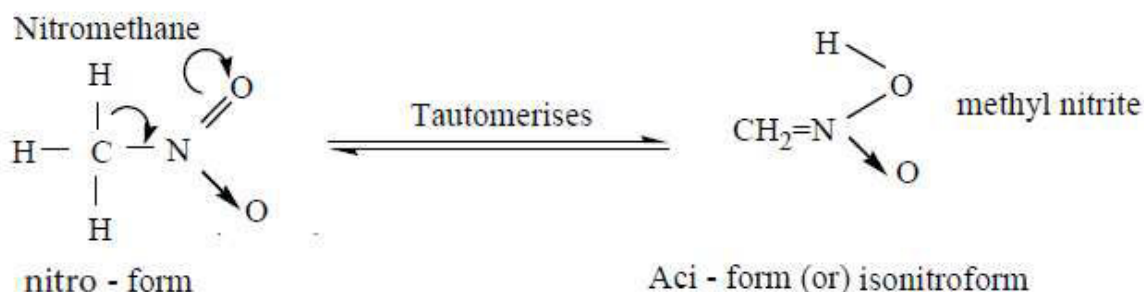
vii) 2- methy-2-nitro propane

viii ) 2-methyl-2-nitroso oxy propane

2. There are two isomers with the formula  $CH_3NO_2$  How will you distinguish between them?

**Tautomerism:**

Primary and secondary nitroalkanes, having  $\alpha$ -H, also show an equilibrium mixture of two tautomers namely nitro and aci- form



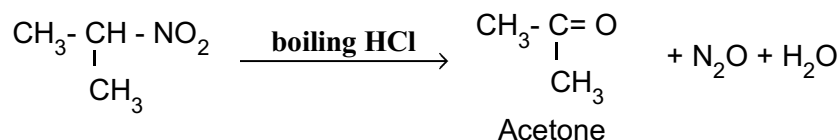
**Distinguish between two form**

S.No.	Nitro form	Aci – form
1.	Less acidic	More acidic and also called pseudoacids (or) nitronic acids
2.	Dissolves in NaOH slowly	Dissolves in NaOH instantly
3.	Decolourises $FeCl_3$ solution	With $FeCl_3$ gives reddish brown colour
4.	Electrical conductivity is low	Electrical conductivity is high

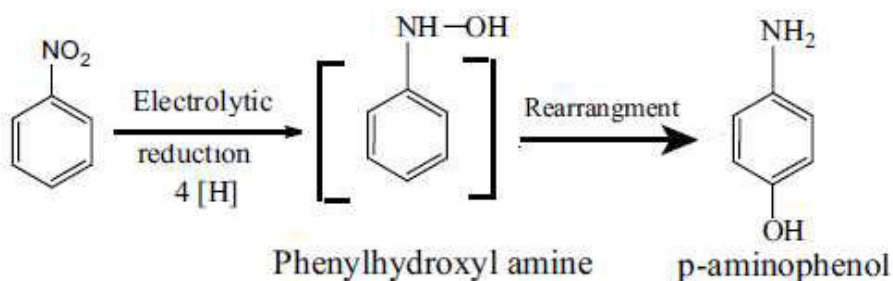
### 3. What happens when

- i. 2 - Nitropropane boiled with HCl
- ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.
- iii. Oxidation of tert - butylamine with  $\text{KMnO}_4$
- iv. Oxidation of acetoneoxime with trifluoroperoxy acetic acid.

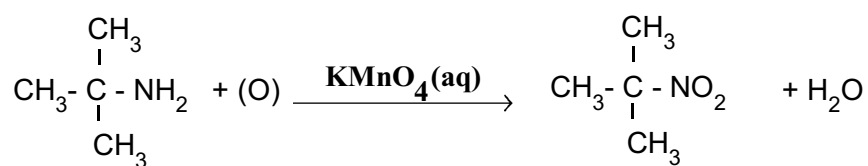
#### i. 2 - Nitropropane boiled with HCl



#### ii. Nitrobenzene undergo electrolytic-reduction in strongly acidic medium.

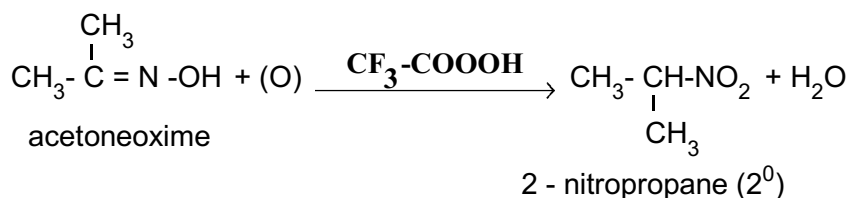


#### ii) Oxidation of tert - butylamine with $\text{KMnO}_4$



#### iv. Oxidation of acetoneoxime with trifluoro peroxy acetic acid.

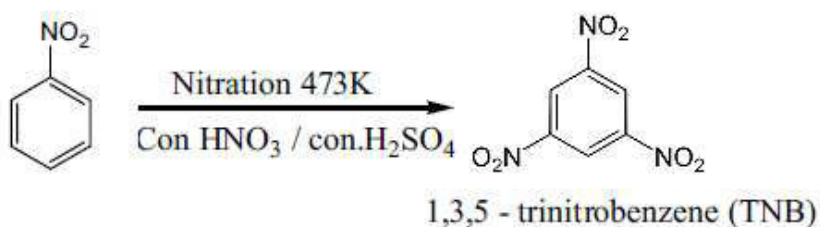
Oxidation of acetoneoxime with trifluoroperoxy acetic acid gives 2 - nitropropane ( $2^0$ ) respectively.

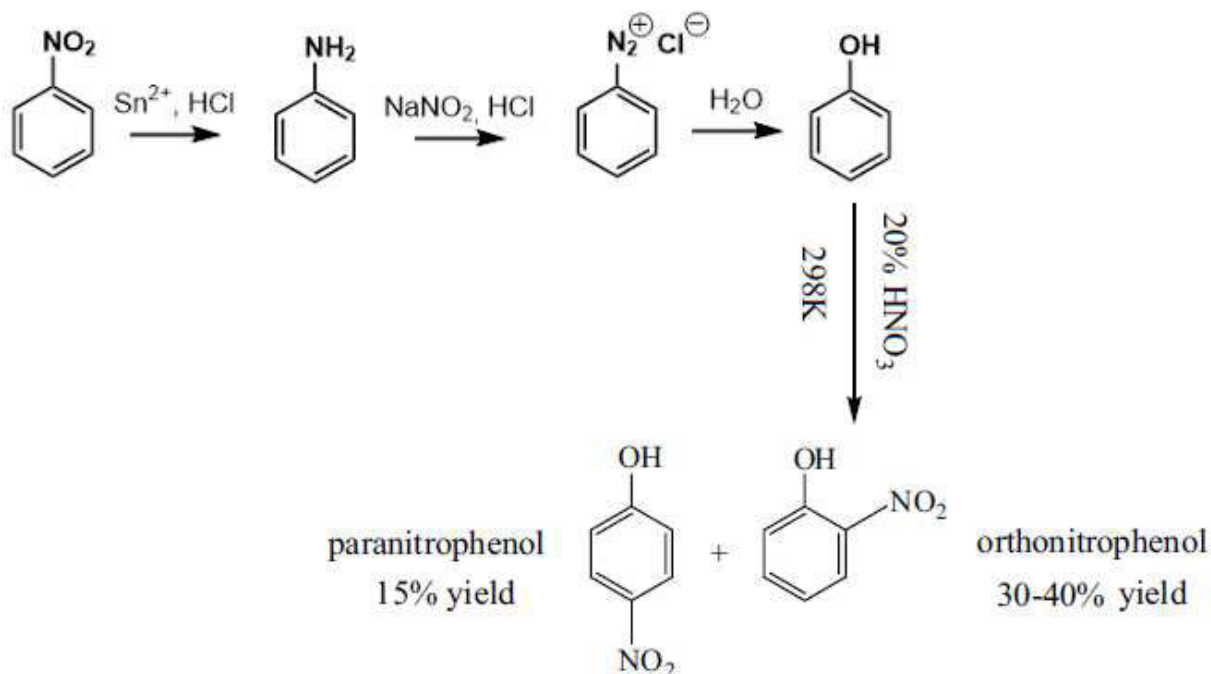
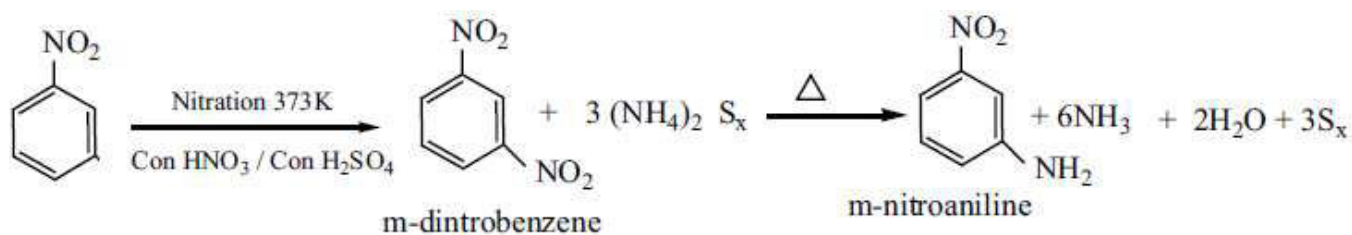
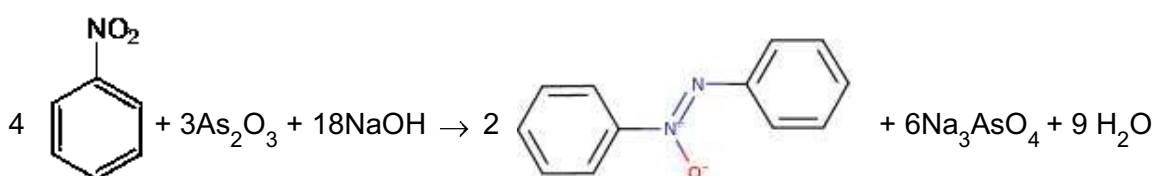
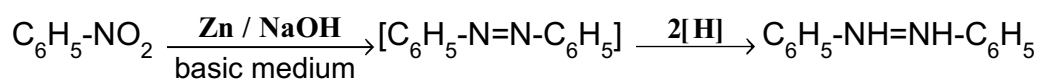
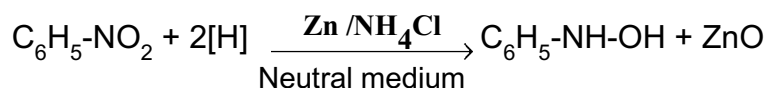
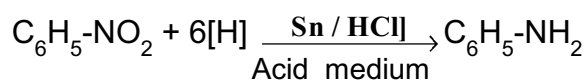


### 4. How will you convert nitrobenzene into

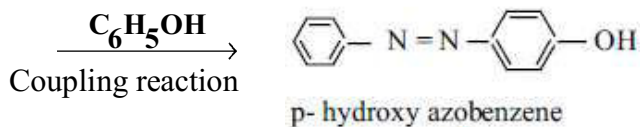
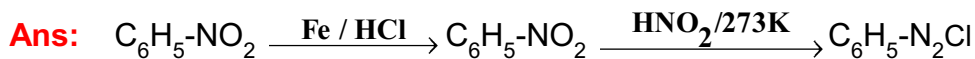
- |                            |                             |
|----------------------------|-----------------------------|
| i. 1,3,5 - trinitrobenzene | ii. o and p- nitrophenol    |
| iii. m - nitro aniline     | iv. azoxybenzene            |
| v. hydrozobenzene          | vi. N - phenylhydroxylamine |
| vii. aniline               |                             |

#### i) Conversion of nitrobenzene into 1,3,5 - trinitrobenzene



**ji Conversion of nitrobenzene into o and p- nitrophenol****iii) Conversion of nitrobenzene into m - nitro aniline****iv) Conversion of nitrobenzene into azoxybenzene hydrozobenzene****iv) Conversion of nitrobenzene into hydrozobenzene****iv) Conversion of nitrobenzene into N - phenylhydroxylamineaniline****iv) Conversion of nitrobenzene into aniline**

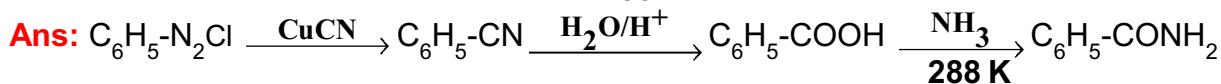
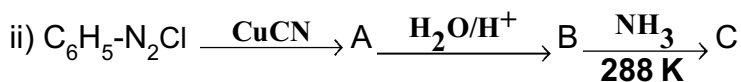
5. Identify compounds A,B and C in the following sequence of reactions.



**A- Aniline**

**B - Benzene diazonium chloride**

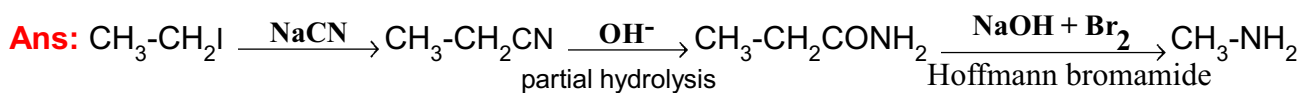
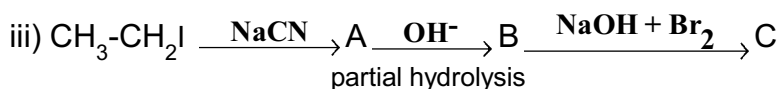
**C - p - hydroxy azobenzene**



**A- Cyanobenzene**

**B - Benzoic acid**

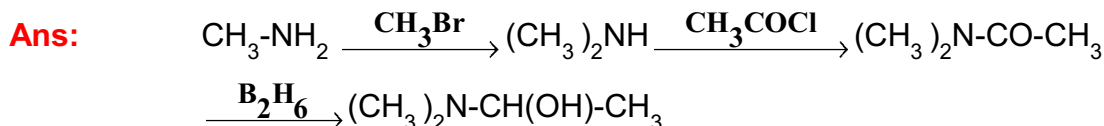
**C - Benzamide**



**A- Ethyl cyanide**

**B - Acetamide**

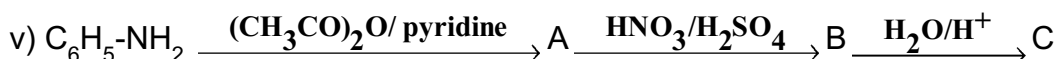
**C - Methyl amine**



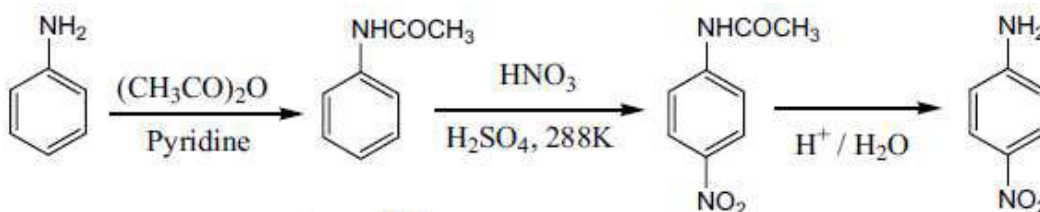
**A- N,N dimethyl amine**

**B - N,N-dimethyl acetamide**

**C - N,N-dimethyl 2- hydroxy ethan amine**



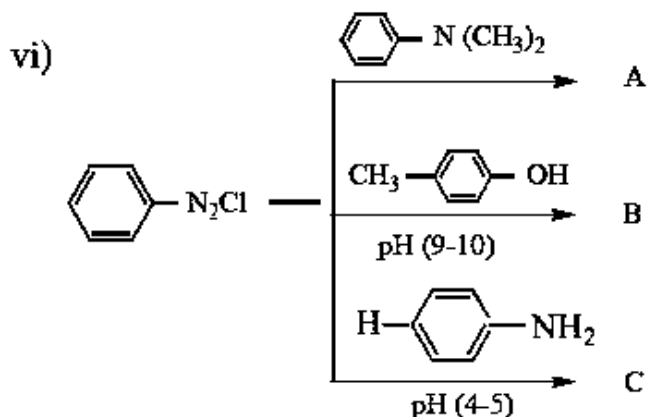
**Ans:**



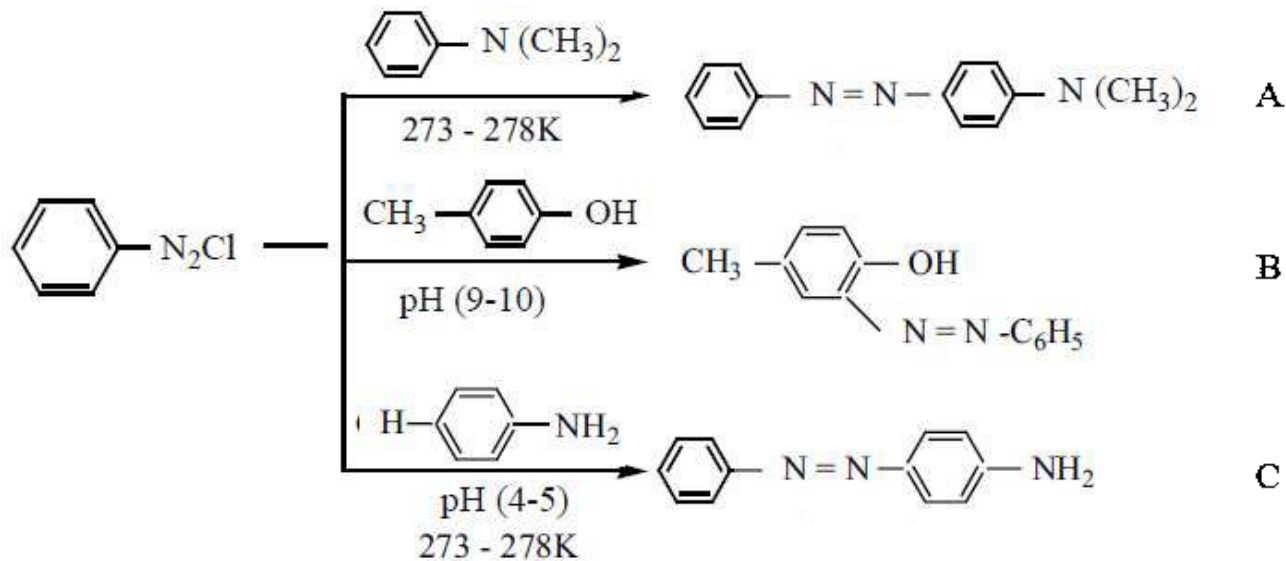
**A - Acetanilide**

**B - p- nitroacetanilide**

**C- p- nitro aniline**



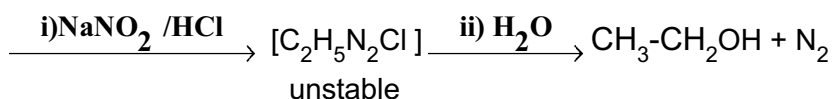
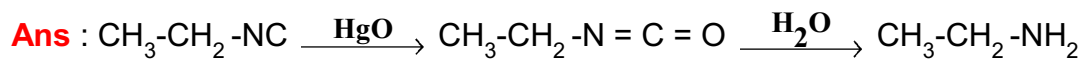
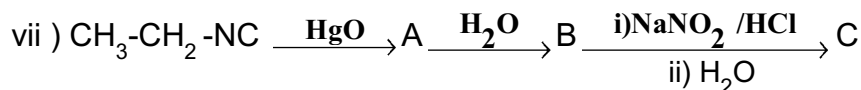
Ans:



A- p-N,N - dimethyl amino azobenzene

B - 2 - phenylazo - 4 -Methyl phenol

C - p - amino azobenzene (Yellow dye)



A- Ethyl iso cyanate

B- Ethyl amine

C- Ethanol

6. Write short notes on the following

i. Hofmann's bromide reaction

ii. Ammonolysis

iii. Gabriel phthalimide synthesis

iv. Schotten - Baumann reaction

v. Carbylamine reaction

vi. Mustard oil reaction

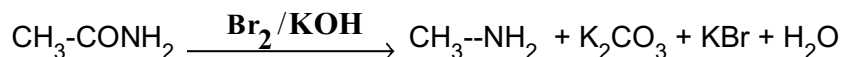
vii. Coupling reaction

viii. Diazotisation

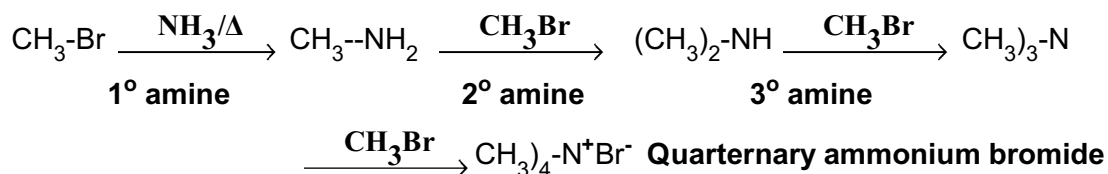
ix. Gomberg reaction

**i. Hofmann's bromide reaction**

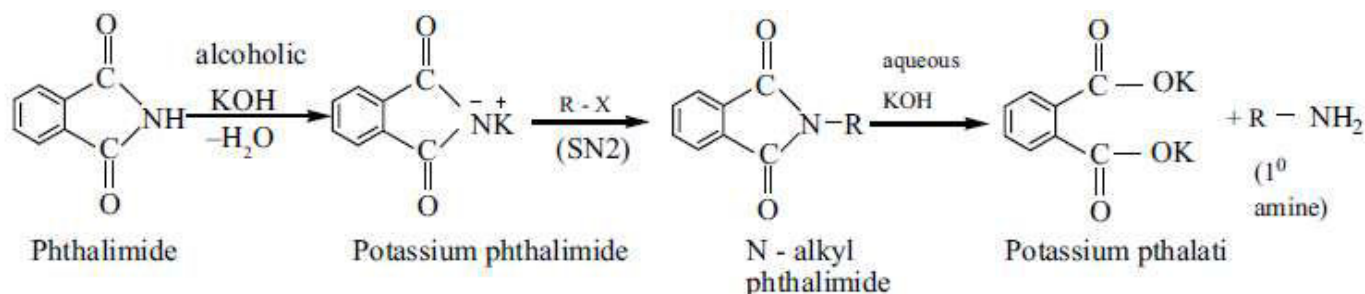
When Amides are treated with bromine in the presence of aqueous or ethanolic solution of KOH, primary amines with one carbon atom less than the parent amides are obtained.

**ii. Ammonolysis**

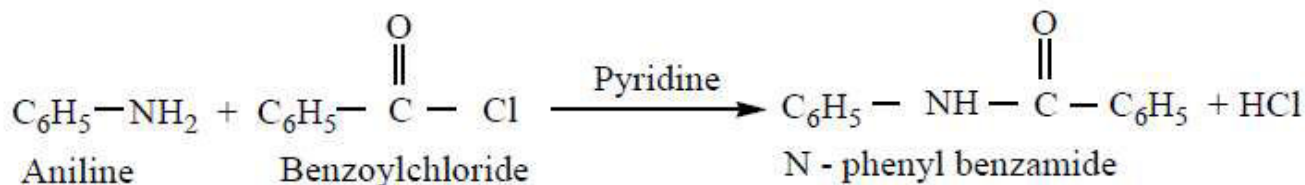
When Alkyl halides (or) benzylhalides are heated with alcoholic ammonia in a sealed tube, mixtures of 1<sup>o</sup>, 2<sup>o</sup> and 3<sup>o</sup> amines and quaternary ammonium salts are obtained

**iii. Gabriel phthalimide synthesis**

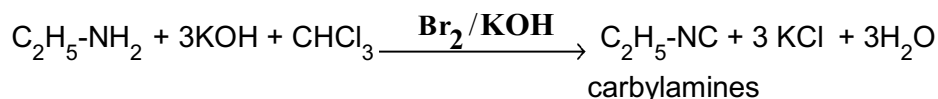
Phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline cannot be prepared by this method because the arylhalides do not undergo nucleophilic substitution with the anion formed by phthalimide

**iv. Schotten - Baumann reaction**

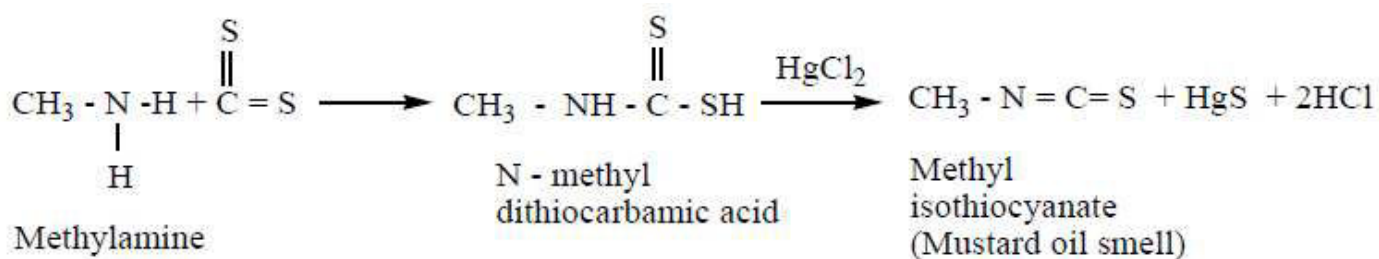
Aniline reacts with benzoylchloride (C<sub>6</sub>H<sub>5</sub>COCl) in the presence of NaOH to give N-phenyl benzamide. This reaction is known as Schotten - Baumann reaction

**v. Carbylamine reaction**

Aliphatic (or) aromatic primary amines react with chloroform and alcoholic KOH to give isocyanides (carbylamines), which has an unpleasant smell. This reaction is known as carbylamines test. This test used to identify the primary amines

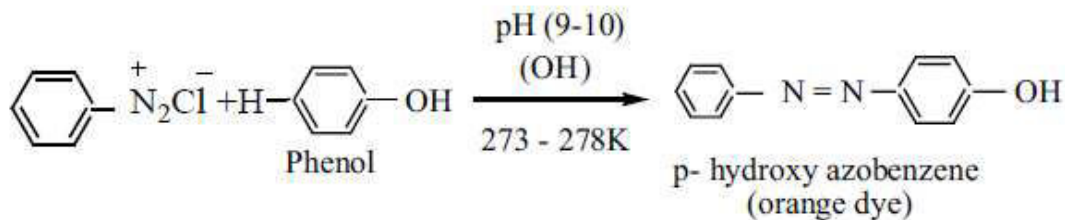
**vi. Mustard oil reaction**

i) When primary amines are treated with carbon disulphide (CS<sub>2</sub>), N - alkyl dithio carbonic acid is formed which on subsequent treatment with HgCl<sub>2</sub>, give an alkyl isothiocyanate.

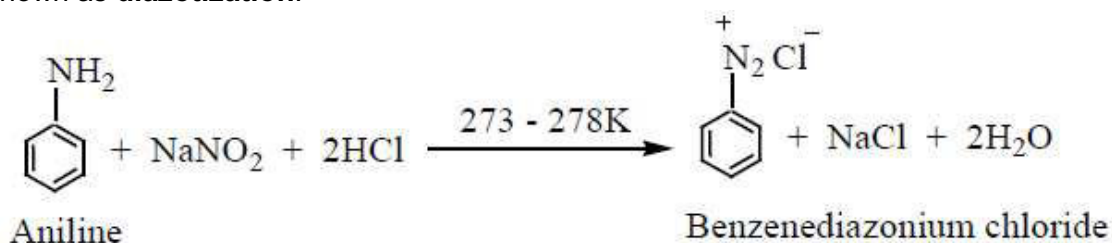


**vii. Coupling reaction**

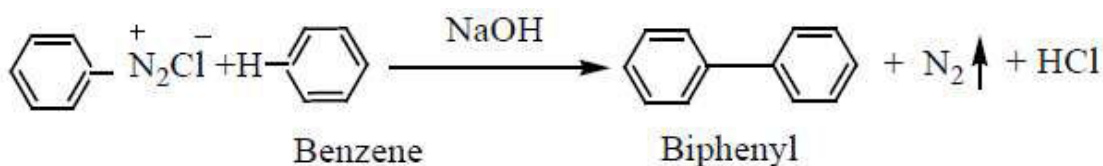
Benzene diazonium chloride reacts with electron rich aromatic compounds like phenol, aniline to form brightly coloured azo compounds.

**viii. Diazotisation**

Aniline reacts with nitrous acid at low temperature (273 - 278 K) to give benzene diazonium chloride which is stable for a short time and slowly decomposes even at low temperatures. This reaction is known as **diazotization**.

**ix. Gomberg reaction**

Benzene diazonium chloride reacts with benzene in the presence of sodium hydroxide to give biphenyl. This reaction is known as the Gomberg reaction.

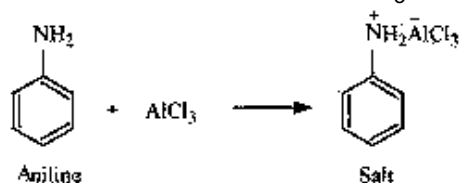
**7. How will you distinguish between primary secondary and tertiary aliphatic amines.**

Reagents	Primary amine	Secondary amine	Tertiary amine
With $\text{HNO}_2$	forms alcohol	N-nitroso amine	forms salt.
With $\text{CHCl}_3/\text{KOH}$	forms carbylamine	No reaction.	No reaction
With $\text{CS}_2$ and $\text{HgCl}_2$	alkyl isothiocyanate is formed	No reaction	No reaction
With Diethyl oxalate	dialkyl oxamide, a solid at room temperature is formed.	Forms N,N-dialkyl oxamic ester, a liquid.	No reaction
With acetyl chloride	forms N-alkyl acetamide.	form N,N-dialkyl acetamide	No reaction



### i. Aniline does not undergo Friedel . Crafts reaction

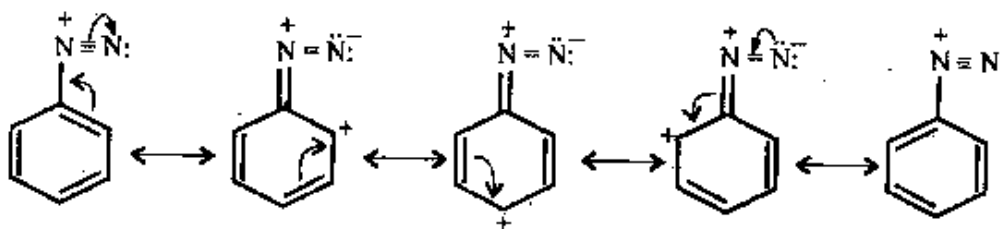
Friedel-Crafts reaction is carried out in the presence of  $\text{AlCl}_3$ . But  $\text{AlCl}_3$  is acidic in nature, while aniline is a strong base. Thus, aniline reacts with  $\text{AlCl}_3$  to form a salt.



Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

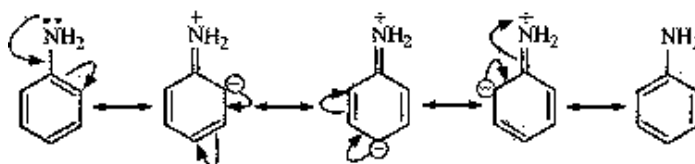
### ii. Diazonium salts of aromatic amines are more stable than those of aliphatic amines

In diazonium salt, the structure goes under resonance due to which the dispersal of positive charge is more and we know that higher is the resonance higher is the stability. Therefore diazonium salt of aromatic amines is more stable than those of aliphatic amines.



### iii. $\text{pK}_b$ of aniline is more than that of methylamine

Aniline undergoes resonance and as a result, the electrons on the N-atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate. On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus,  $\text{pK}_b$  of aniline is more than that of methylamine.

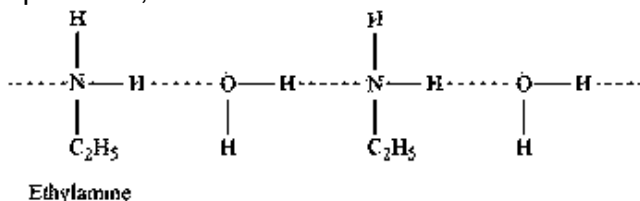


### iv. Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Gabriel phthalimide synthesis results in the formation of  $1^\circ$  amine only.  $2^\circ$  or  $3^\circ$  amines are not formed in this synthesis. Thus, a pure  $1^\circ$  amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

### v. Ethylamine is soluble in water whereas aniline is not

Ethylamine when added to water forms intermolecular H-bonds with water. And therefore it is soluble in water. But aniline does not form H-bond with water to a very large extent due to the presence of a large hydrophobic  $-\text{C}_6\text{H}_5$  group. Hence, aniline is insoluble in water.



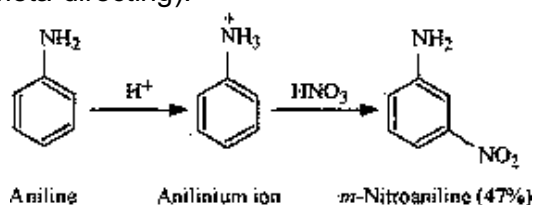
### vi. Amines are more basic than amides

The lone pair of electrons on the amine are more available to accept a proton and act as a base. This is because in amides, the carbonyl ( $\text{C}=\text{O}$ ) group is highly electronegative, so has a greater power to draw electrons towards it, making the lone pair of the amide nitrogen less available to accept a proton.



**vii. Although amino group is o - and p - directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m- nitroaniline**

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing).

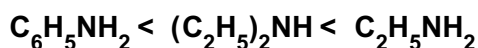


For this reason, aniline on nitration gives a substantial amount of m-nitroaniline.

**9. Arrange the following**

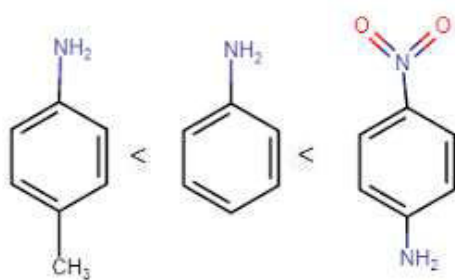
**i. In increasing order of solubility in water,  $C_6H_5NH_2$ ,  $(C_2H_5)_2NH$ ,  $C_2H_5NH_2$**

The more extensive the H-bonding, the higher is the solubility. Thus,  $C_2H_5NH_2$  undergoes more extensive H-bonding than  $(C_2H_5)_2NH$ . Hence, the solubility in water of  $C_2H_5NH_2$  is more than that of  $(C_2H_5)_2NH$ .



**ii. In increasing order of basic strength**

**a) aniline, p-toluidine and p-nitroaniline**

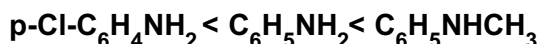


In p-toluidine, the presence of electron-donating  $-CH_3$  group increases the electron density on the N-atom. Thus, p-toluidine is more basic than aniline.  $-NO_2$  group decreases the electron density over the N-atom in p-nitroaniline. Thus, p-nitroaniline is less basic than aniline.

**b) In increasing order of basic strength  $C_6H_5NH_2$ ,  $C_6H_5NHCH_3$ , p-Cl- $C_6H_4NH_2$ ,**

i) Chlorine atom has both - I effect and + R effect so para chloro aniline is less basic than aniline

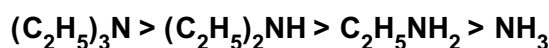
$CH_3$ - group is electron donating group in so increases electron density in N - atom so, N - Methyl aniline is more basic than aniline



**iii. In decreasing order of basic strength in gas phase**

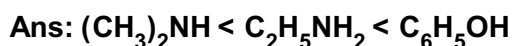


In gas phase there is no hydrogen bonding, therefore stabilisation due to hydrogen bonding is not there. Therefore the only effect to determine the strength is the inductive effect. The +I effect increases with increase in the alkyl group. Therefore the basic strength will be the highest in  $(C_2H_5)_3N$  and least in  $NH_3$ . Therefore the decreasing order of basic strength in gas phase will be



**iv. In increasing order of boiling point  $C_6H_5OH$ ,  $(CH_3)_2NH$ ,  $C_2H_5NH_2$**

The electronegativity of O is more than N. Therefore  $C_6H_5OH$  forms hydrogen bonding and because of the hydrogen bonding the alcohols will have higher boiling point than the amines with comparable molecular mass. Now between  $(CH_3)_2NH$  and  $C_2H_5NH_2$ ,  $C_2H_5NH_2$  has more hydrogen atom attached to the Nitrogen. Therefore the extent of hydrogen bonding will be more in primary amines i.e.  $C_2H_5NH_2$  as compared to sec or ter amines. Therefore  $C_2H_5NH_2$  will have higher boiling point as compared to  $(CH_3)_2NH$ . Therefore the increasing order of boiling point will be as given below.

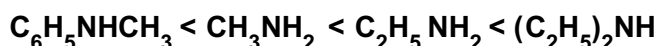


**v. In decreasing order of the  $pK_b$  values  $C_2H_5NH_2$ ,  $C_6H_5NHCH_3$ ,  $(C_2H_5)_2NH$  and  $CH_3NH_2$**

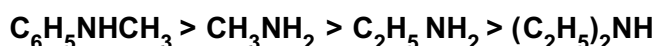
**Larger the value of  $K_b$  or smaller the value of  $pK_b$ , stronger is the base.**

(i) In  $C_2H_5NH_2$ , only one  $-C_2H_5$  group is present while in  $(C_2H_5)_2NH$ , two  $-C_2H_5$  groups are present. Thus, the +I effect is more in  $(C_2H_5)_2NH$  than in  $C_2H_5NH_2$ . Therefore, the electron density over the N-atom is more in  $(C_2H_5)_2NH$  than in  $C_2H_5NH_2$ . Hence,  $(C_2H_5)_2NH$  is more basic than  $C_2H_5NH_2$ .

ii) In  $C_6H_5NHCH_3$  is less basic than  $(C_2H_5)_2NH$  and  $C_2H_5NH_2$  due to the delocalization of the lone pair in the former two. Further, among  $C_6H_5NHCH_3$  the former will be more basic due to the +I effect of  $-CH_3$  group. Hence, the order of increasing basicity of the given compounds is as follows:



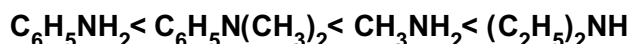
**We know that the higher the basic strength, the lower is the  $pK_b$  values.**



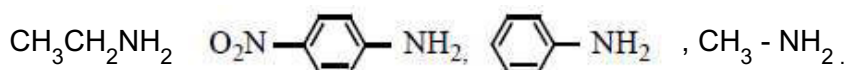
**vi. Increasing order of basic strength  $C_6H_5NH_2$ ,  $C_6H_5N(CH_3)_2$ ,  $(C_2H_5)_2NH$  and  $CH_3NH_2$**

$C_6H_5N(CH_3)_2$  is more basic than  $C_6H_5NH_2$  due to the presence of the +I effect of two  $-CH_3$  group in  $C_6H_5N(CH_3)_2$ . Further  $CH_3NH_2$  contains one  $-CH_3$  group while  $(C_2H_5)_2NH$  contains two  $-C_2H_5$  group. Thus,  $(C_2H_5)_2NH$  is more basic than  $CH_3NH_2$ .

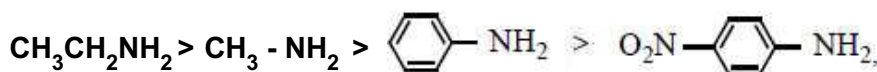
Now  $C_6H_5N(CH_3)_2$  is less basic than  $CH_3NH_2$  because of the -R effect of  $-C_6H_5$  group. Hence, the increasing order of the basic strength of the given compounds is as follows



**vii. In decreasing order of basic strength**

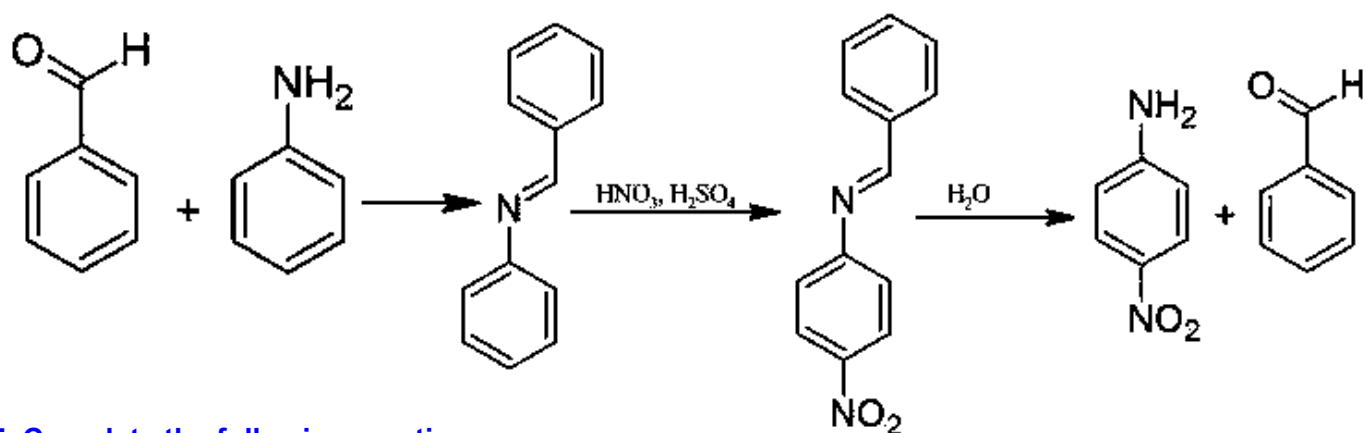
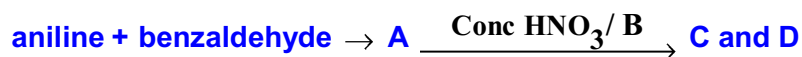


Aliphatic amines are more basic than aromatic amines. so  $CH_3CH_2NH_2$  and  $CH_3-NH_2$  are more basic.  $CH_3CH_2NH_2$  is more +I effect than  $CH_3-NH_2$ , so  $CH_3CH_2NH_2$  more basic than  $CH_3-NH_2$ . In case of substituted aniline, electron withdrawing group like  $-NO_2$ , they have both -R effect as well as -I effect. as result all nitro amines are weaker bases than aniline.

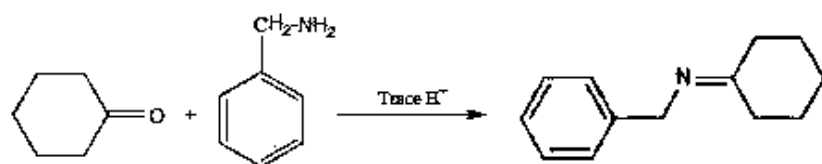




14. Identify A, B, C and D

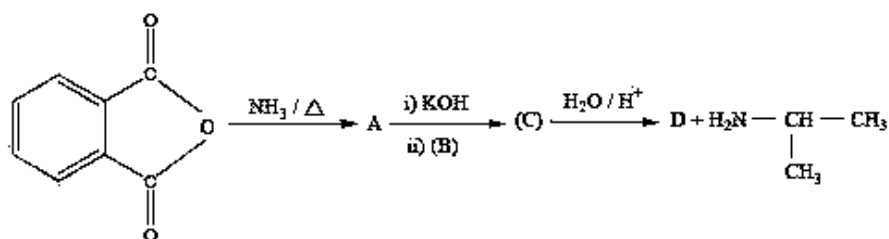


15. Complete the following reaction

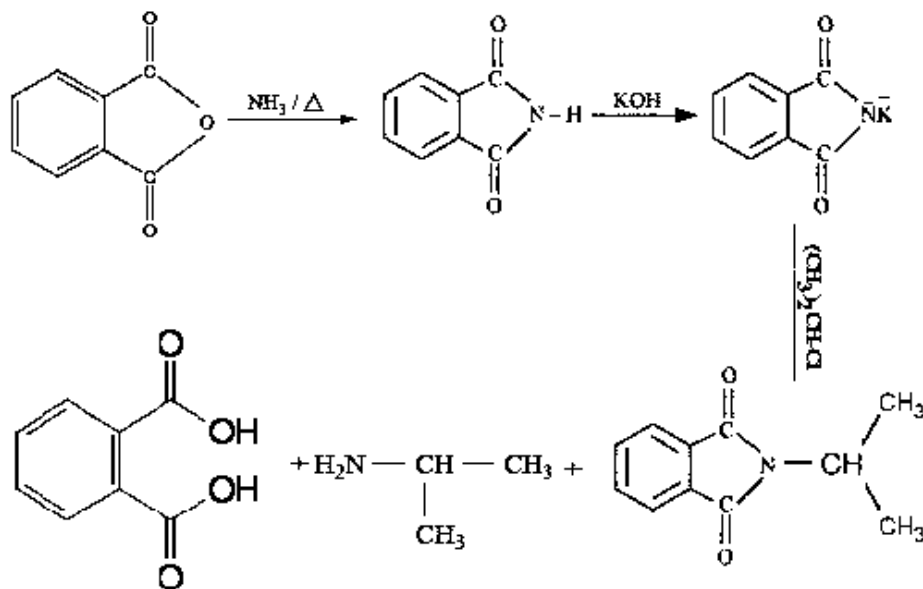


N-benzyl cyclo hexane imine

16. Predict A, B, C and D for the following reaction



Ans:



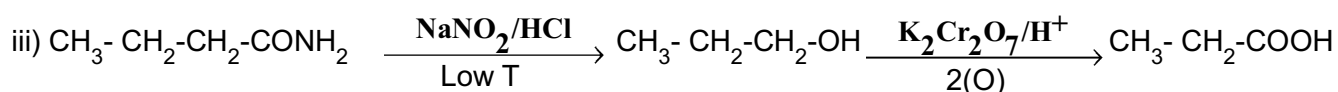
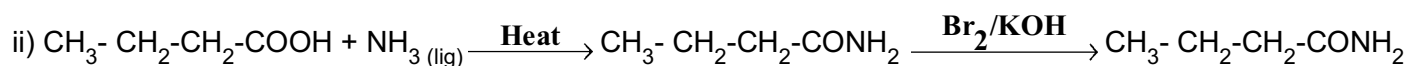
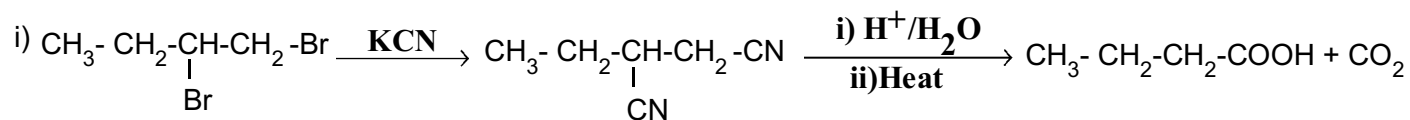
A- phthalimide

B - 2-Chloropropane

C- N- isopropyl phthalimide

D- phthalic acid

17. A dibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of  $\text{CO}_2$ . (B) on heating with liquid ammonia followed by treating with  $\text{Br}_2/\text{KOH}$  gives (c) which on treating with  $\text{NaNO}_2$  and  $\text{HCl}$  at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74. Identify A to D.



A - 1,2 - dibromo butane

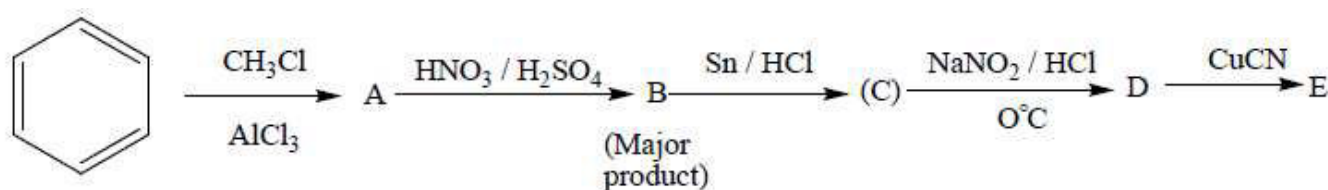
B - 1,2 dicyano butane

C - 1 - amino propan

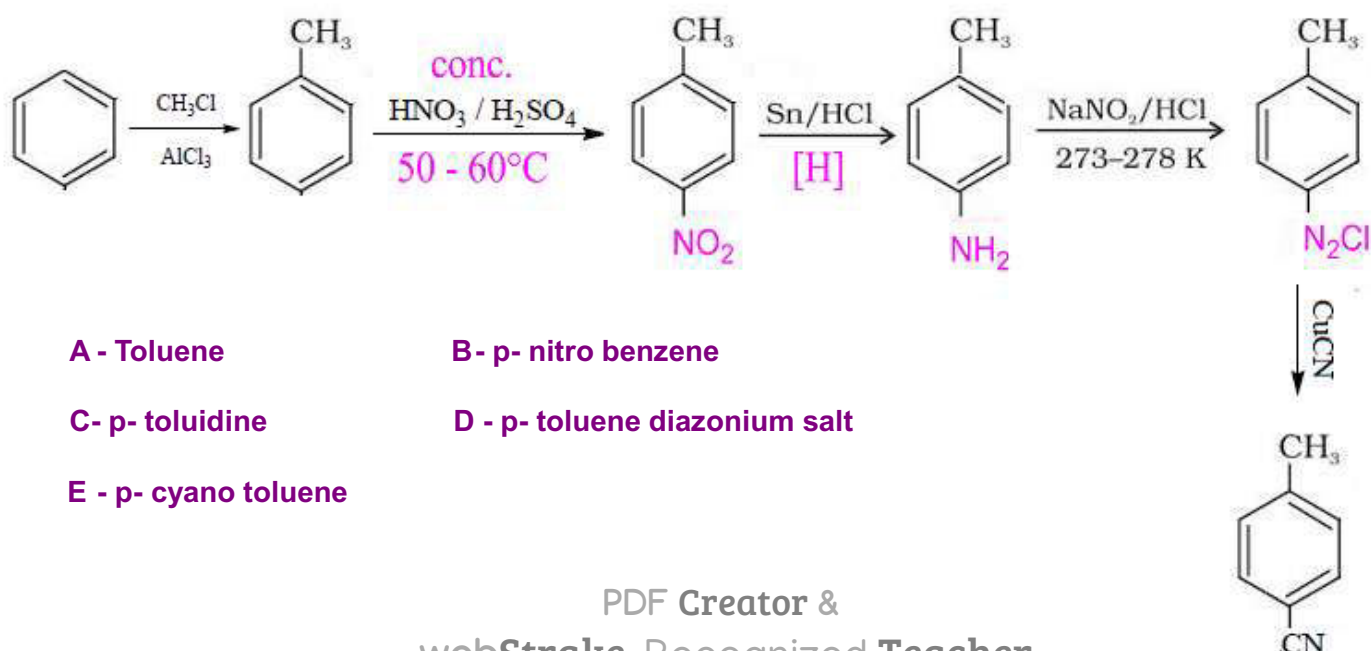
D - Propanoic acid

Molecular mass of propanoic acid - 74

18. Identify A to E in the following frequency of reactions.



Ans:



A - Toluene

B - p- nitro benzene

C - p- toluidine

D - p- toluene diazonium salt

E - p- cyano toluene