Chapter 13
Organic Nitrogen Compounds

I. Choose the Correct Answer

Question 1.
Which of the following reagent can be used to convert nitrobenzene to aniline
a) Sn/HCl
b) ZnHg/NaOH
c) $LiAlH_4$
d) All of these
Answer:
a) Sn/HCl

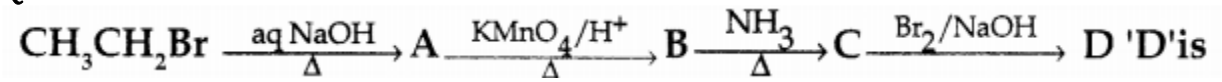
Question 2.
The method by which aniline cannot be prepared is
a) degradation of benzamide with Br_2/NaOH
b) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.
c) Hydrolysis of phenylcyanide with acidic solution.
d) reduction of nitrobenzene by Sn/HCl
Answer:
b) potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

Question 3.
Which one of the following will not undergo Hofmann bromamide reaction
a) $CH_3CONHCH_3$
b) $CH_3CH_2CONH_2$
c) CH_3CONH_2
d) $C_6H_5CONH_2$
Answer:
a) $CH_3CONHCH_3$
Solution: Only primary amides undergo Hofmann bromamide reaction

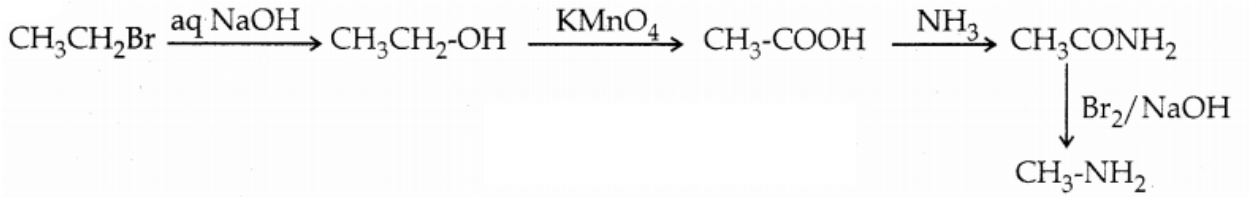
Question 4.
Assertion: Acetamide on reaction with KOH and bromine gives acetic acid
Reason: Bromine catalyses hydrolysis of acetamide.
a) if both assertion and reason are true and reason is the correct explanation of assertion
b) if both assertion and reason are true but reason is not the correct explanation of assertion.
c) assertion is true but reason is false

d) both assertion and reason are false
Answer:
d) both assertion and reason are false.

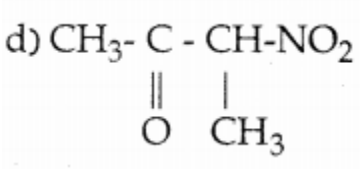
Question 5.



a) bromomethane
b) α -Bromo sodium acetate
c) methanamine
d) acetamide
Answer:
c) methanamine
Solution:



Question 6.
Which one of the following nitro compounds does not react with nitrous acid?
a) CH_3-CH_2-CH_2-NO_2
b) $(CH_3)_2$ CH-CH_2 NO_2
c) $(CH_3)_3CNO_2$



Answer:
c) $(CH_3)_3CNO_2$
Solution:
3^0 Nitroalkane

Question 7.
Aniline + benzoylchloride $\xrightarrow{NaOH}$ C_6H_5-NH-COC_6H_5 this reaction is known as
a) Friedel – Crafts reaction
b) HVZ reaction
c) Schotten – Baumann reaction
d) None of these
Answer:
c) Schotten – Baurnann reaction

Question 8.
The product formed by the reaction of an aldehyde with a primary amine (NEET)
a) carboxylic acid
b) aromatic acid
c) Schiff's base
d) ketone
Answer:
c) Schiff's base

Question 9.
Which of the following reaction is not correct

a) $CH_3CH_2NH_2 \xrightarrow{HNO_2} CH_3CH_2OH + N_2$

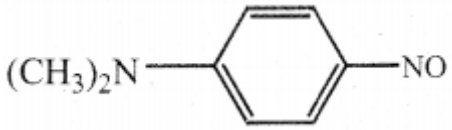
b) $(CH_3)_2N-C_6H_5 \xrightarrow{NaNO_2/HCl} (CH_3)_2N-C_6H_4-N=NCl$

c) $CH_3CONH_2 \xrightarrow{Br_2/NaOH} CH_3NH_2$

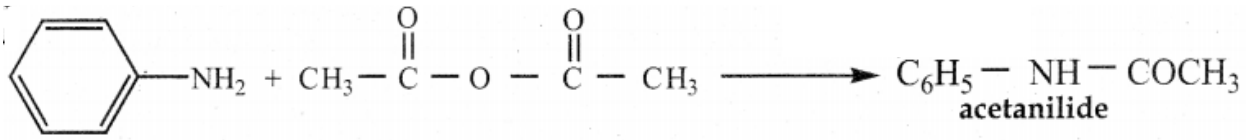
d) None of these
Answer:

b) $(CH_3)_2N-C_6H_5 \xrightarrow{NaNO_2/HCl} (CH_3)_2N-C_6H_4-N=NCl$

Solution:
p – nitrosation takes places, the product is im7



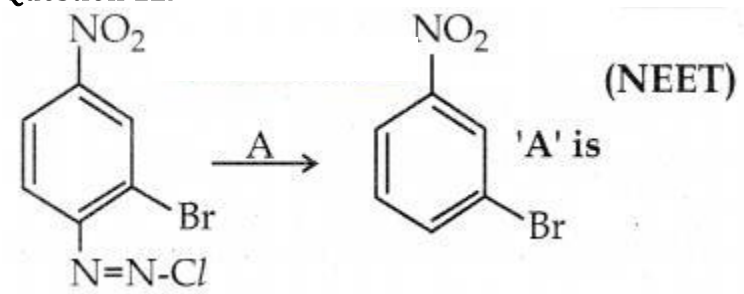
Question 10.
When aniline reacts with acetic anhydride the product formed is
a) o – amirìoacetophenone
b) m – aminoacetophenone
c) p – aminoacetophenone
d) acetanilide
Answer:
d) acetanilide
Solution:



Question 11.
The order of basic strength for methyl substituted amines in aqueous solution is

a) $N(CH_3)_3 > N(CH_3)_2H > N(CH_3)H_2 > NH_3$
b) $N(CH_3)H, > N(CH_3)_2H > N(CH_3)_3 > NH_3$
c) $NH_3 > N(CH_3)H_2 > N(CH_3)_2H > N(CH_3)_3$
d) $N(CH_3)_2H > N(CH_3)H_2 > N(CH_3)_3 > NH_3$
Answer:
d) $N(CH_3)_2H > N(CH_3)H_2 > N(CH_3)_3 > NH_3$

Question 12.



(NEET)

'A' is

a) H_3PO_2 and H_2O
b) H^+/H_2O
c) $HgSO_4$ / H_2SO_4
d) Cu_2Cl_2
Answer:
a) H_3PO_2 and H_20

Question 13.

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{NaNO_2/HCl} B \xrightarrow[283K]{H_2O} C$$ 'C' is

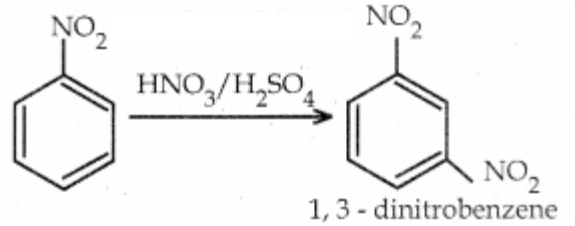
a) C_6H_5-OH
b) C_6H_5-CH_2OH
c) C_6H_5-CHO
d) $C_6H_5NH_2$
Answer:
a) C_6H_5-OH
Solution:

$$C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2 \xrightarrow{NaNO_2/HCl} C_6H_5N_2Cl \xrightarrow{H\ O} C_6H_5\text{-}OH + N_2 + HCl$$

Question 14.
Nitrobenzene on reaction with Con HNO_3 / H_2SO_4 at 80- 100°C forms which one of the following products?
a) 1, 4 – dinitrobenzene
b) 2, 4, 6 – tirnitrobenzene
c) 1, 2 – dinitrobenzene
d) 1, 3 – dinitrobenzene
Answer:

d) 1, 3 -dinitrobenzene

Solution:



Question 15.

$C_5H_{13}N$ reacts with HNO_2 to give an optically active compound – The compound is

a) pentan-1 -amine

b) pentan-2-amine

c) N, N – dimethyipropan -2-amine

d) N-methylbutan-2-amine

Answer:

d) N-methylbutan-2-amine

Question 16.

Secondary nitro alkanes react with nitrous acid to form

a) red solution

b) blue solution

c) green solution

d) yellow solution

Answer:

b) blue solution

Question 17.

Which of the following amines does not undergo acetylation?

a) t-butylamine

b) ethylamine

c) diethylamine

d) triethylamine

Answer:

d) triethylamine (3^oamine)

Question 18.

Which one of the following is most basic?

a) 2, 4 – dichloroaniline

b) 2, 4 – dimethylaniline

c) 2, 4 – dinitroaniline

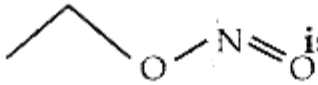
d) 2, 4 – dibromoaniline

Answer:

b) 2,4-dimethylaniline

Solution: CH_3 is a+I group, all other – I group +T group increase the electron density on NH_2 and hence increase the basis nature.

Question 19.

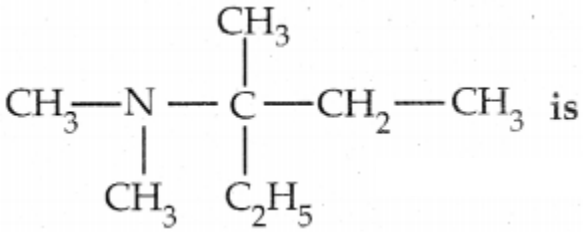
When  is reduced with Sn / HCI the pair of compounds formed are

a) Ethanol, hydroxylamine hydrochloride
b) Ethanol, ammonium hydroxide
c) Ethanol, NH_2OH
d) $C_3H_5NH_2$, H_2O

Answer:
a) Ethanol, hydroxylamine hydrochloride

Question 20.

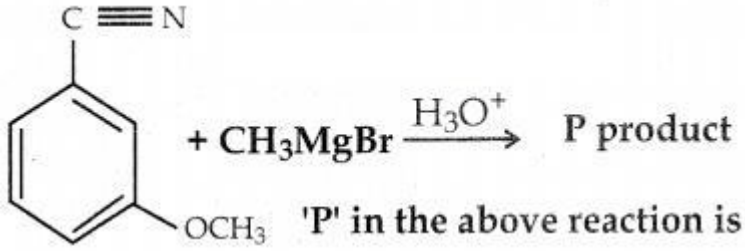
UPAC name for the amine

 is

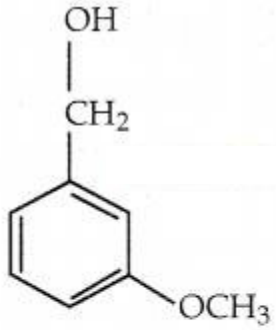
a) 3 – Bimethy lamino – 3 – methyl pentane
b) 3(N,N – Triethyl) – 3 – amino pentane
c) 3-N,N – trimethyl pentanamine
d) 3 – (N,N – Dimethyl amino) – 3- methyl pentane

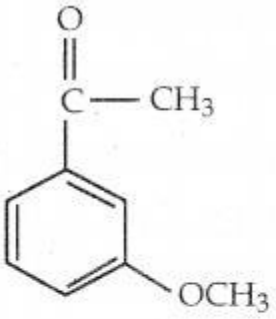
Answer:
d) 3 – (N,N – Dimethyl amino) -3- methyl pentane

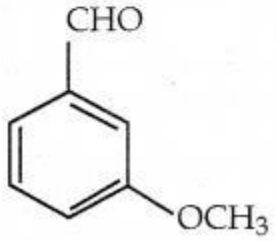
Question 21.

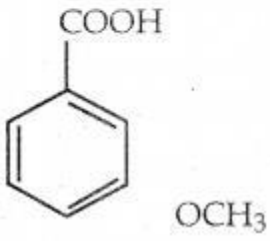


'P' in the above reaction is

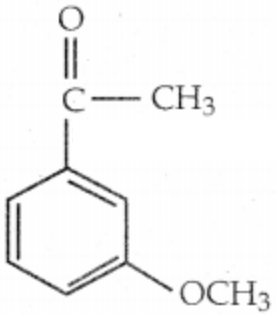
a) 

b) 

c) 

d) 

Answer:

b) 

Question 22.

Ammonium salt of benzoic acid is heated strongly with P_2O_5 and the product so formed is reduced and then treated with $NaNO_2$/ HCl at low temperature. The final compound formed is

a) Benzene diazonium chloride
b) BenzYl alcohol
c) Phenol
d) Nitrosobenzene

Answer:

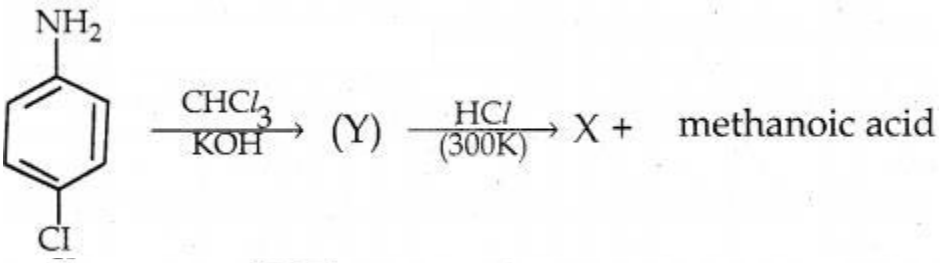
b) Benzyl alcohol

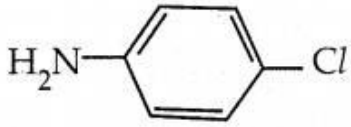
Solution:

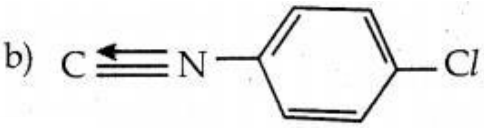
$$C_6H_5COONH_4 \xrightarrow[\Delta]{P_2O_5} C_6H_5 - C \equiv N \xrightarrow{LiAlH_4} C_6H_5CH_2NH_2 \xrightarrow{HNO_2} C_6H_5CH_2OH$$

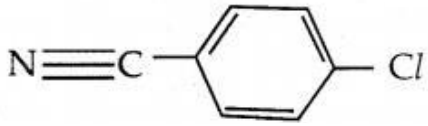
Question 23.

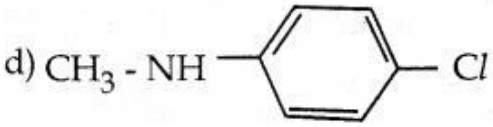
Identify X in the sequence given below.



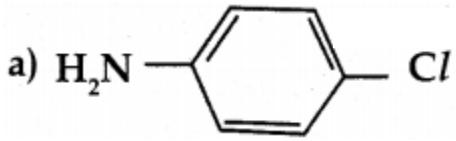
a) 

b) 

c) 

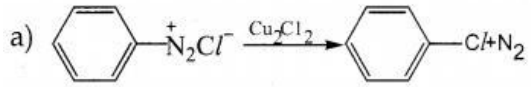
d) 

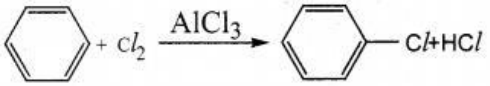
Answer:

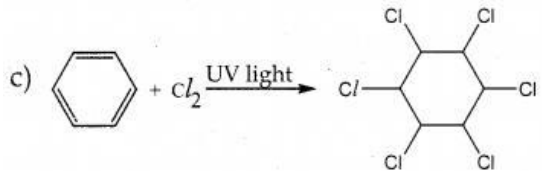
a) 

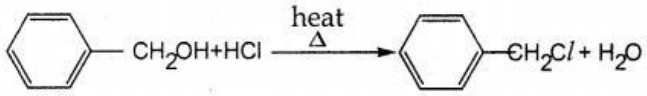
Question 24.

Among the following, the reaction that proceeds through an electrophilic substitution, is:

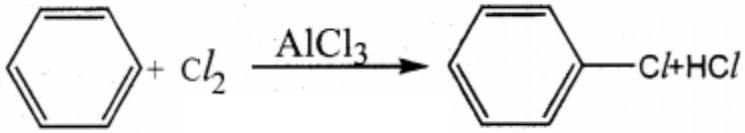
a) 

b) 

c) 

d) 

Answer:

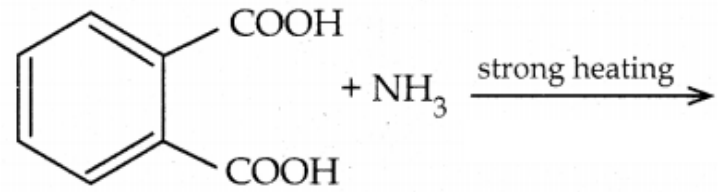
b) 

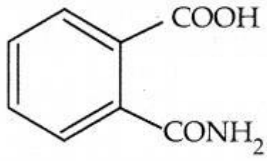
Explanation:

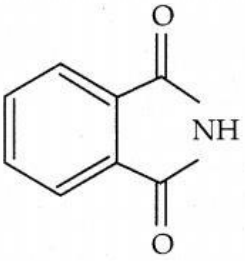
a) Nucleophilic substitution
b) Electrophilic substitution
c) Addition Reaction
d) Nucleophilic substitution

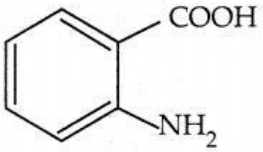
Question 25.

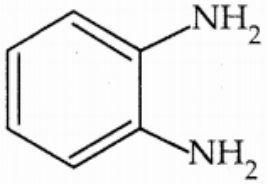
The major product of the following reaction



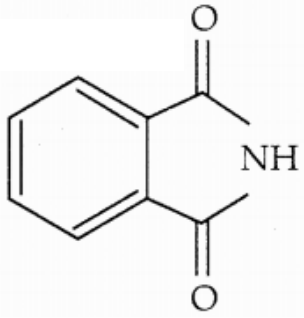
a) 

b) 

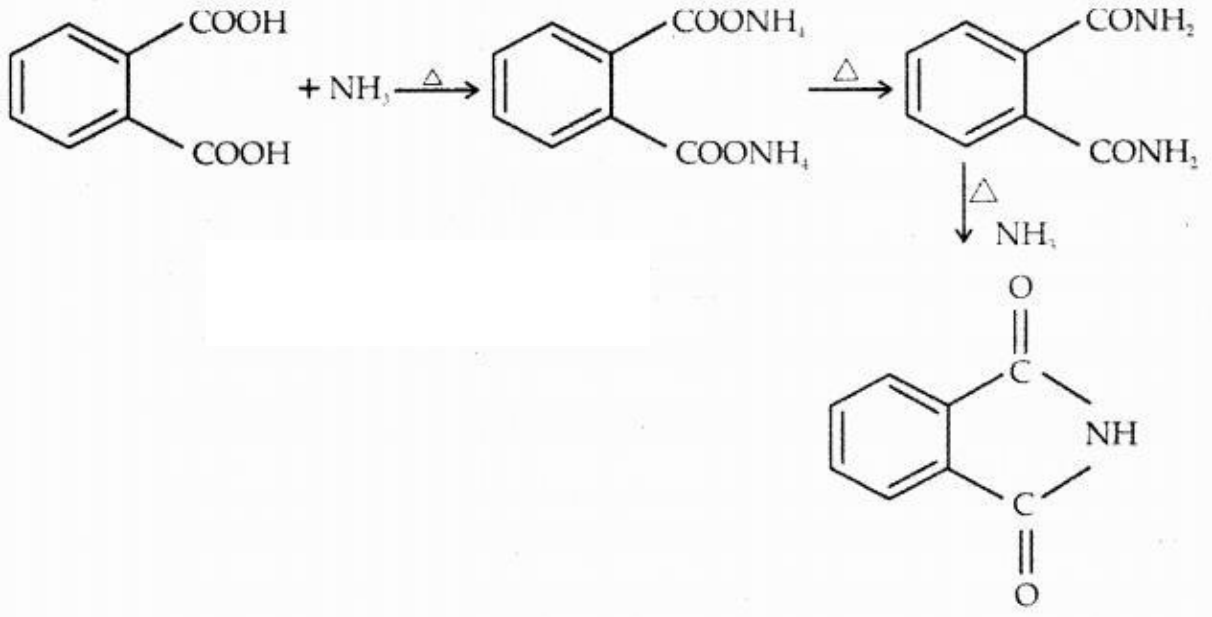
c) 

d) 

Answer:

b) 

Solution:



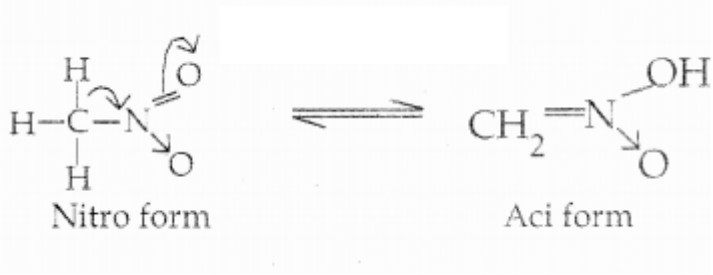
II. Short Answer Questions

Question 1.
Write down the possible isomers of the $C_4H_9NO_2$ and give their IUPAC names
Answer:

S.No	Isomer	IUPAC Name
1.	$CH_3-CH_2-CH_2-CH_2-NO_2$	1-nitro butane-
2.	$CH_3-CH_2-\underset{\displaystyle NO_2}{\underset{\vert}{CH}}-CH_3$	2- nitro butane
3.	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-NO_2$	2-methyl-1-nitropropane
4.	$CH_3-CH_2-CH_2-CH_2-O-N=O$	Butylnitrite (or) 1-nitroso oxybutane
5.	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-O-N=O$	2- methyl propylnitrite
6.	$CH_3-CH_2-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-COOH$	2- aminobutanoic acid
7.	$CH_3-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-CH_2-COOH$	3- aminobutanoic acid
8.	$H_2N-CH_2-CH_2-CH_2-COOH$	4- aminobutanoic acid
9.	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle NH_2}{\overset{\vert}{C}}}}-COOH$	2 - amino-2-methyl propanoic acid
10.	$H_2N-CH_2-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-COOH$	3 – amino–2–methyl propanoic acid
11.	$CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{N}}-CH_2-COOH$	2 - (dimethylamino) ethanoic acid

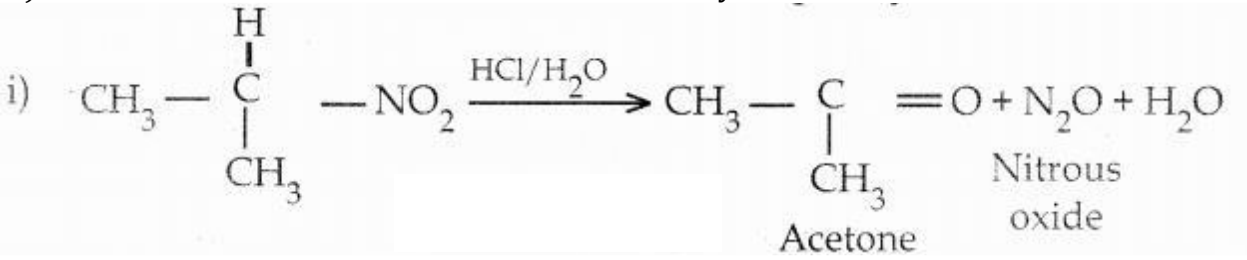
Question 2.
There are two isomers with the formula CH_3NO_2. How will you distinguish between them?
Answer:

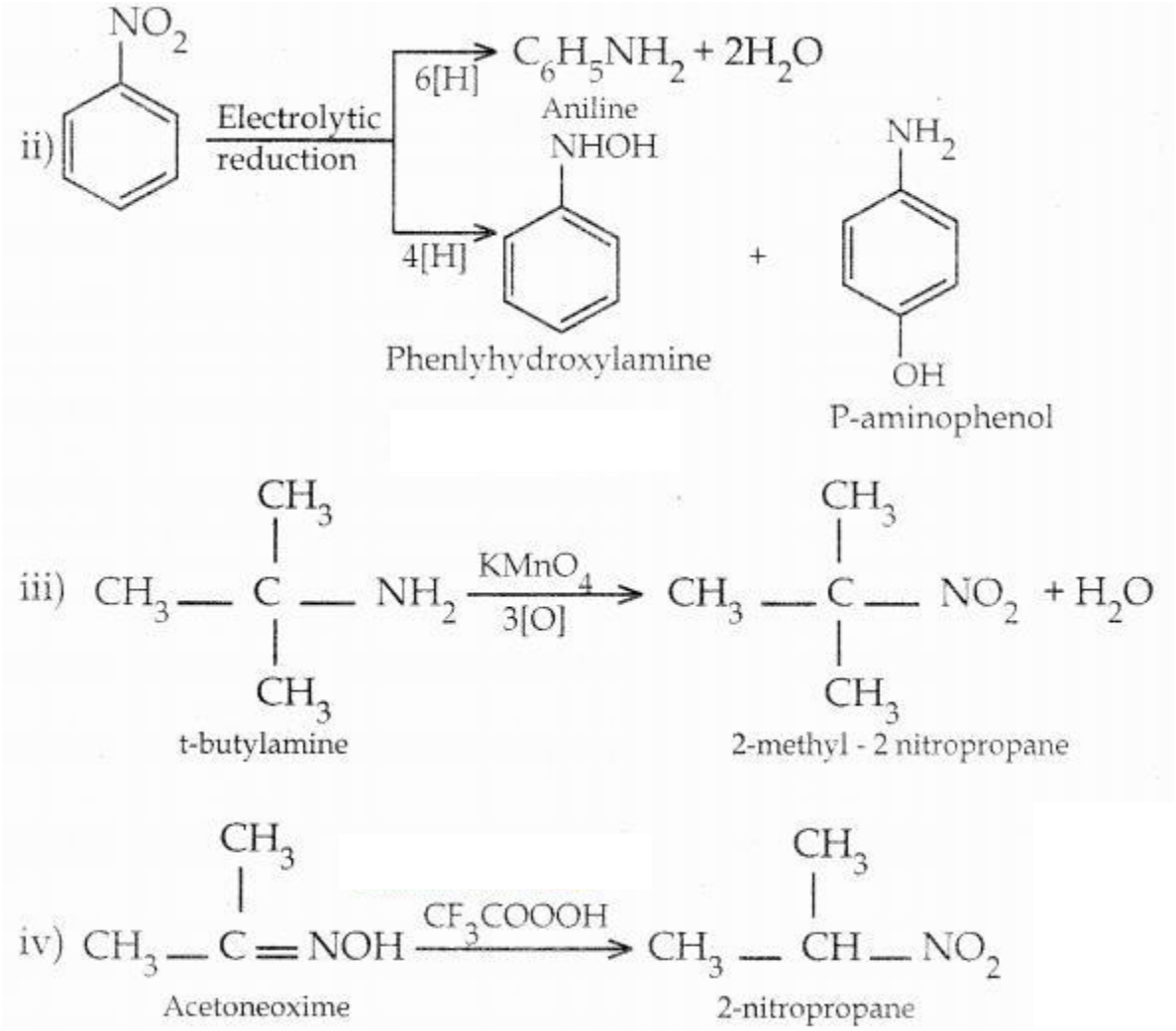
- Primary and secondary nitroalkanes with a-H atom exhibit tautomerism.
- Tertiary amines do not exhibit tautomerism due to CH =N the absence of a-H atom.
- Nitromethane exists in two tautomeric forms namely \itro form Aci form nitroform and aciform.



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. Decoiourises $FeCl_3$ Solution	With $FeCl_3$, gives reddish-brown colour
4. Electrical conductivity is low	Electrical conductivity is high

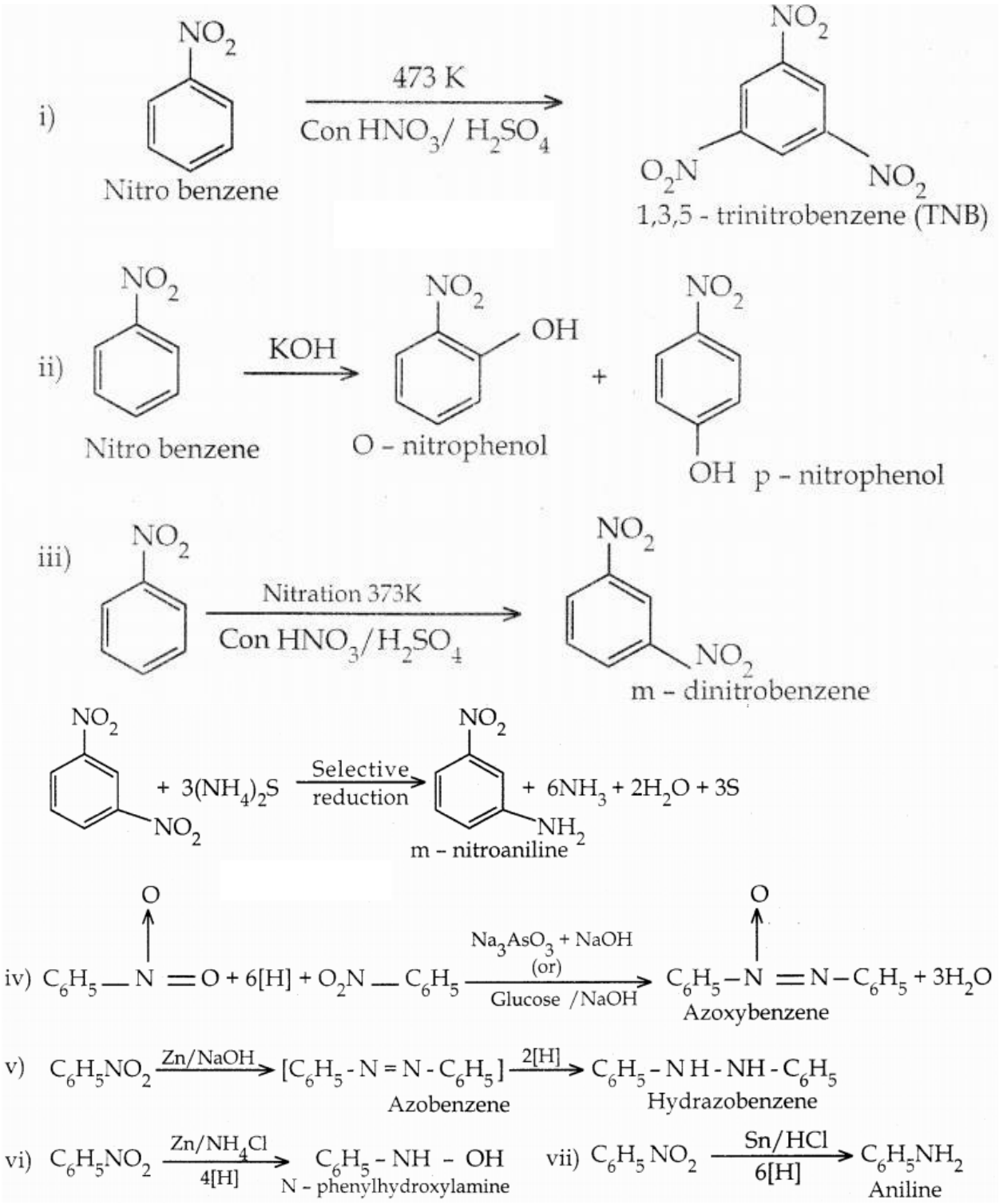
Question 3.
What happens when
Answer:
i) 2 – Nitropropane boiled with HCl
ii). Nitrobenzene electrolytic reduction in strongly acidic medium.
iii). Oxidation of tert – butylamine with $KMnO_4$
iv). Oxidation of acetone oxime with trifluoromethoxy acetic acid.





Question 4.
How will you convert nitrobenzene into
Answer:

- 1, 3, 5 – trinitrobenzene
- o and p – nitrophenol
- m – nitro aniline
- azoxvbenzcne
- hvdrazohenzene
- N – phenvl hyd roxylamine
- aniline



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

i) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow{C_6H_5OH} C$

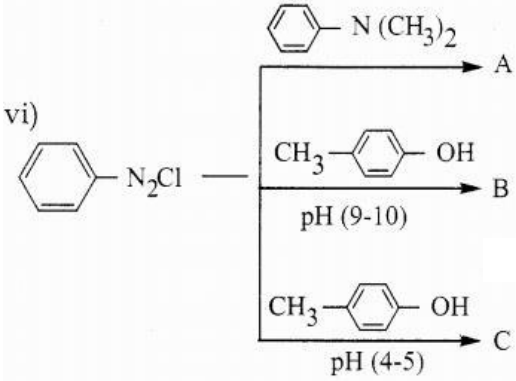
ii) $C_6H_5N_2Cl \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$

iii) $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial hydrolysis}]{OH^-} B \xrightarrow{NaOH+Br_2} C$

iv) $CH_3NH_2 \xrightarrow{CH_3Br} A \xrightarrow{CH_3COCl} B \xrightarrow{B_2H_6} C$

v) $C_6H_5NH_2 \xrightarrow[\text{pyridine}]{(CH_3CO)_2O} A \xrightarrow[H_2SO_4,288K]{HNO_3} B \xrightarrow{H_2O/H^+} C$

vi)

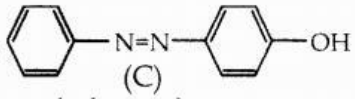


vii) $CH_3CH_2NC \xrightarrow{HgO} A \xrightarrow{H_2O} B \xrightarrow[ii)H_2O]{i)NaNO_2/HCl}$

(i) $C_6H_5NO_2 \xrightarrow{Fe/HCl} C_6H_5NH_2 \xrightarrow[273K]{HNO_2} C_6H_5-N=N-Cl$

(A) Aniline

(B) Benzenediazonium Chloride

$\xrightarrow{C_6H_5OH}$ 

(C) p-hydroxyazobenzene

(ii) $C_6H_5N_2Cl \xrightarrow[KCN]{CuCN} C_6H_5CN \xrightarrow{H_2O/H^+} C_6H_5COOH \xrightarrow{NH_3} C_6H_5COONH_4$

(A) Phenylcyanide — (B) Benzoic acid — (C) Ammonium benzoate

(iii) $CH_3CH_2I \xrightarrow{NaCN} CH_3CH_2CN \xrightarrow[\text{Partial hydrolysis}]{OH^-} CH_3CH_2CONH_2 \xrightarrow[NaOH]{Br_2} CH_3CH_2NH_2$

(A) Ethylcyanide — (B) Propanamide — Hoffmann's degradation — (C) Ethylamine

iv) CH_3NH_2 (Methylamine) $\xrightarrow{CH_3Br}$ CH_3NHCH_3 (A) (N – Methyl methanamine) $\xrightarrow{CH_3COCl}$ $CH_3CON(CH_3)_2$ (B) (N, N-dimethylacetamide)

$\xrightarrow{B_2H_6}$ $CH_3-CH(OH)-N(CH_3)_2$ (C)

1-(hydroxy-N, N-dimethyl) ethanamine.

v) Aniline (NH_2) $\xrightarrow[\text{Pyridine}]{(CH_3CO)_2O}$ Acetanilide ($NHCOCH_3$) (A) $\xrightarrow[H_2SO_4,\ 288K]{HNO_3}$ + (B) p- nitroacetanilide ($NHCOCH_3$, NO_2)

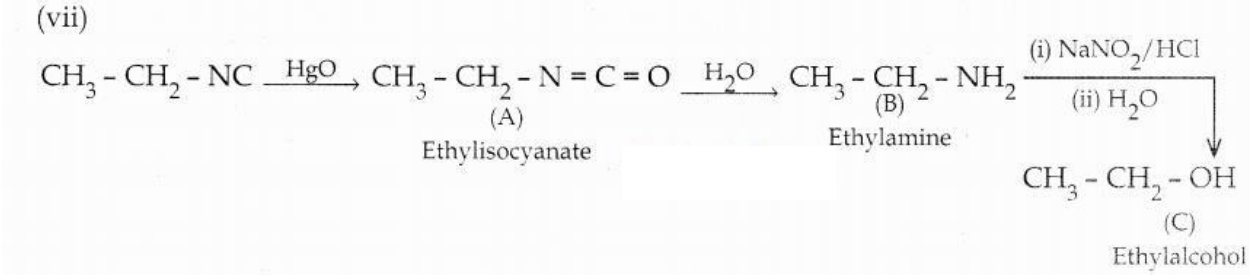
$\xrightarrow{H^+/H_2O}$ p- nitroaniline (NH_2, NO_2)

vi) $C_6H_5N_2Cl$ + $C_6H_5N(CH_3)_2$ → p- N - N dimethyl amino azobenzene ($C_6H_5N=NC_6H_4N(CH_3)_2$)

+ $CH_3C_6H_4OH$, pH(9-10) → (A) 2 – Phenylazo – 4 –methylphenol ($CH_3C_6H_3(OH)N=NC_6H_5$)

+ $C_6H_5NH_2$, pH(4–5) → (B) p - aminoazo benzene ($C_6H_5N=NC_6H_4NH_2$) (C)

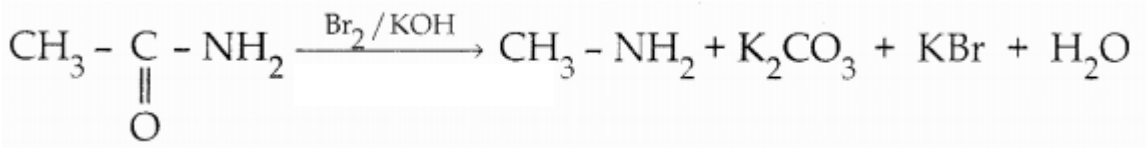
(vii)



Question 6.
Write short notes on the following
Answer:

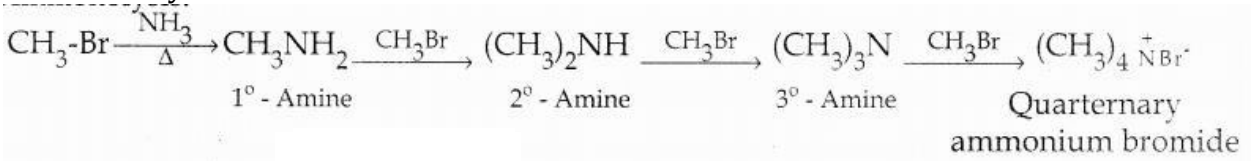
- Hofmann's bromide reaction
- Ammonolysis
- Gabriel phthalimide synthesis
- Schotten – Baurnann reaction
- Carhvlamine reaction
- Mustard oil reaction
- Coupling reaction
- Diazotisation
- Gorenberg reaction

I Hofmann's bromamide reaction:



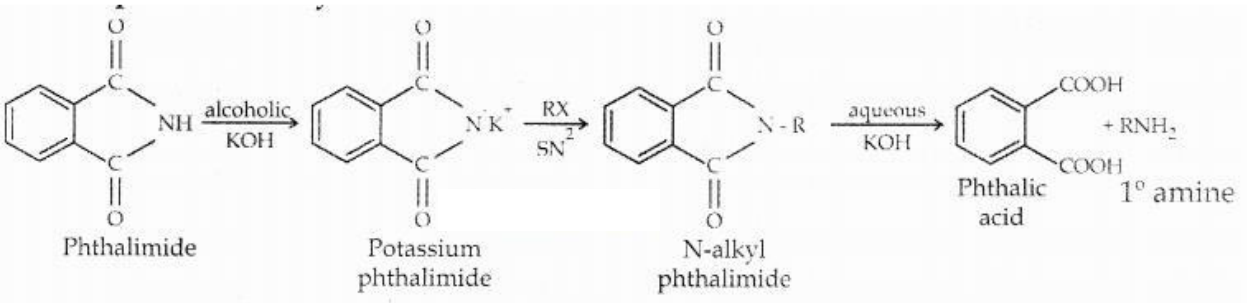
In Hofnianns degradation acid amide is converted into an amine with one carbon less by Br_2/ KOH.

ii. Ammonolysis:



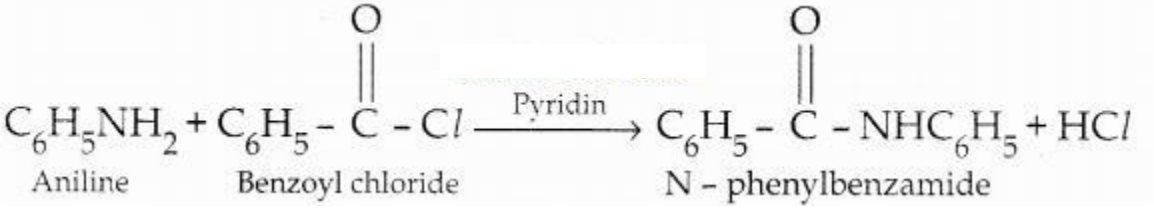
In Hoffmann's ammonolysis alkyl halides are heated with alcoholic ammonia in a sealed tube, mixtures of 1°, 2° and 3° amines and quarternary ammonium salts are obtained.

iii. Gabriel phthalimide synthesis



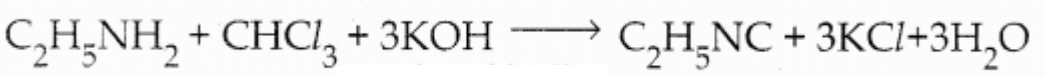
Phthalimide on treatment with alcoholic KOH forms potassium phthalimide which on heating with alkyl halide followed by alkaline hydrolysis gives primary amine. Aniline can not be prepared by this method.

iv. Schotten – Baumann reaction:



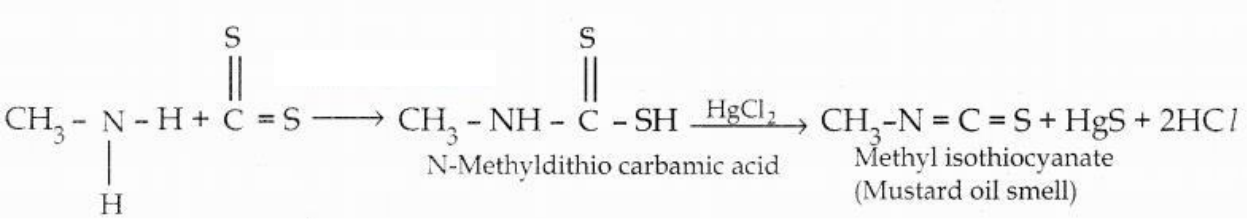
Benzoylation of amines to give N-alkyl benzamide in presence of NaOH is known as Schotten Baumann reaction.

v. Carbylamine reaction



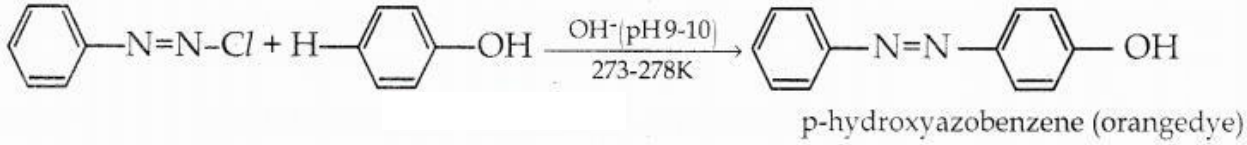
Primary' amines react with chloroform and alcoholic KOH to form isocyanides called carbylamines with unpleasant smell. This is used to identify primary amines.

vi. Mustard oil reaction



When primary amines are treated with carbon disulphide, N-alkyl dithiocarbamic acid is formed which on treatment with $HgCl_2$ gives an alkyl isothiocyanate.

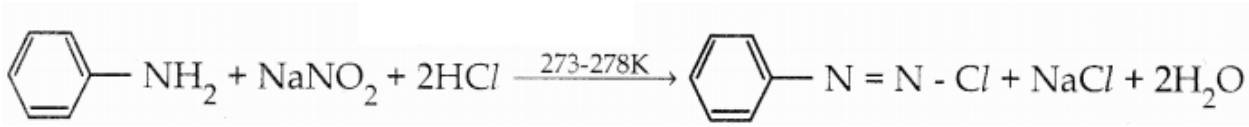
vii. Coupling reaction:



Benzenediazonium chloride reacts with electron-rich aromatic compounds like phenol,

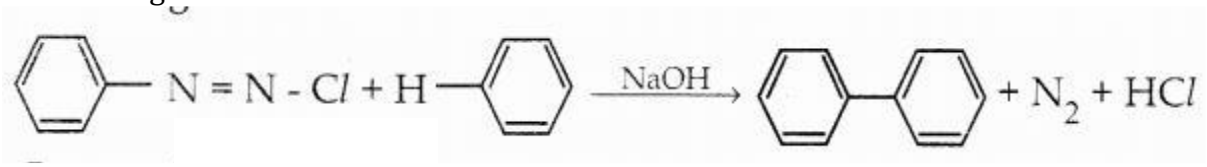
undergoing
electrophilic substitution at para position.

viii. Diazotisation:



Aniline reacts with nitrous acid at 273-278K to form benzene diazonium chloride.

ix. Gomberg reaction:



Benienediazonium chloride reacts with benzene in presence of NaOH to give biphenyl.

Question 7.
How will you distinguish between Primary, Secondary, and tertiary aliphatic amines
Answer:

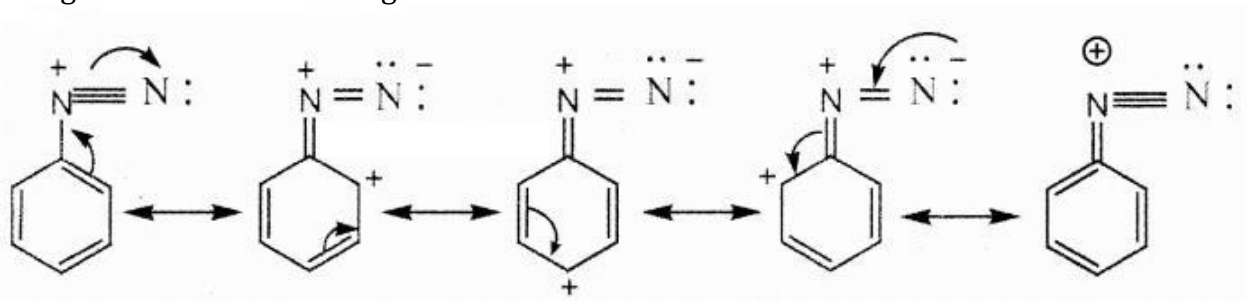
S.No	Reaction with	Primary amine	Secondary amine	Tertiary amine
1	HNO_2	forms alcohol	forms N-nitroso amine	forms salt
2	$CHCl_3/KOH$	forms carbylamine	no reaction	no reaction
3	acetylchloride	forms N - alkyl acetamide	forms N,N - dialkyl acetamide	no reaction
4	$CS_2/HgCl_2$	forms alkyl isothiocyanate	no reaction	no reaction
5	Alkyl halide	forms quarternary ammonium salt with three moles of alkylhalide	forms quartenary ammonium salt with two moles of alkylhalide	forms quarternary ammonium salt with one mole of alkyl halide
6	Diethyloxalate	forms solid dialkyloxamide	forms liquid N,N - dialkyl oxamic ester	no reaction

Question 8.
Account for the following
Answer:

- Aniline does not undergo Friedel – Crafts reaction
- Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- pK_b of aniline is more than that of methylamine
- Gabriel phthalimide synthesis is preferred for synthesising_primary amines
- Ethvlamine is soluble in water whereas aniline is not
- Amines are more basic than amides
- Although amino group is o – and p – directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m – nitroaniline.

i) Aniline does not undergo Friedel – crafts reaction, because Aniline is basic in nature
Aniline donates its lone pair to the lewis acid $Alcl_3$ to form an adduct which inhibits further electrophilic substitution reaction

ii) The stability of diazonium salts of aromatic amines is due to the dispersal of the positive charge over the benzene ring.



iii) In aniline the NH
group is directly attached to the benzene ring.
The lone pair of electron on nitrogen atom in aniline gets delocalised over the benzene ring.
Hence it is less available for protonation.
So aniline is less basic than methylamine and pK_b of aniline is more than that of methylamine.

iv) Gabriel phthalimide synthesis results in the formation of primary amines only.
Secondary and tertiary amines are not formed in this synthesis. Thus a pure primary amine can be obtained.
Therefore, Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

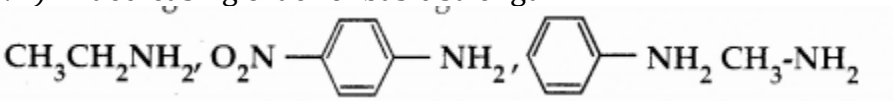
v) Ethvlamine forms intermolecular hydrogen bonds with water. Hence it is soluble in water.
But aniline does not form hydrogen bond with water to a very large extent due to the presence of a large hydrophobic C_6H_5 – group. Hence aniline is insoluble in water

vi) In amides the carbonyl group $(C = 0)$ is highly electronegative and draws the electrons towards it.
This makes the lone pair of amide nitrogen less available to accept a proton.
Hence amides are less basic than amines.

But in amines the alkyl groups being electron releasing groups. the electron pair on amine nitrogen is readily available to accept a proton.

vii) Hence amines are more basic than amides.
In strong acid medium aniline is protonated to form anilinium ion which is rn-directing. Hence a substantial amount of rn-nitroaniline is formed during nitration of aniline.

Question 9.
Arrange the following
Answer:
i) In increasing order of solubility in water $C_6H_5NH_2$,$(C_2H_5)_2NH$,$C_2H_5NH_2$
ii) In increasing order of basic strength
a) aniline, p – toludine and p – nitroaniline
b) $C_6H_5NH_2$ $C_6H_5NHCH_3$, $C_6H_5NH_2$, p-Cl-C_6H_4-NH_2
iii) In decreasing order of basic strength in gas phase
$(C_2H_5)NH_2$, $(C_2H_5)NH$, $(C_2H_5)_3N$ and NH_3
iv) In increasing order of boiling point C_6H_5OH, $(CH_3)_2NH$,$C_2H_5NH_2$
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
vi) Increasing order of basic strength $C_6H_5NH_2$, $C_6H_5N(CH_3)$ $H_53)_2$, $(C_2H_5)_2$ NH and CH_3 NH_2
vii) In decreasing order of basic strength



i) Increasing order of solubility in water $C_6H_5NH_2 < (C_2H_5)$ NH $< C_2H_5$ NH_2
Hint
Aromatic amine
aliphatic amine
Solubility $\alpha \frac{1}{\text{Molarmass}}$

ii) Increasing order of basic strength
a) p-nitro aniline
aniline
p-toludine
b) p – Cl- C_6H_4– $NH_2 < C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5NH_2$
Hint > p-nitrogroup (-I) electron with drawing, hence decreases the basic strength.
Hint > p-methyl group (+I) electron releasing, hence increases the basic strength.

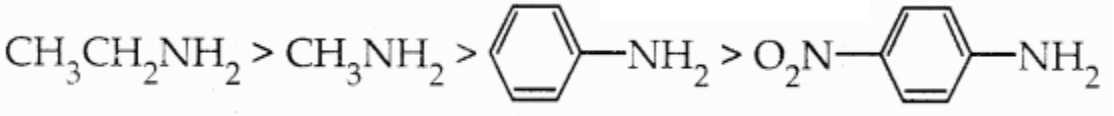
iii) Decreasing order of basic strength in gas phase
$(C_2H_5)_3N > (C_2H_5)_2$ NH > C_2H_5 $NH_2 > NH_3$
Hint > In the gas-phase there is no solvation effect. As a result the basic strength mainly depends on the + I effect. Higher the number of alkyl groups higher will be the +1 effect, stronger is the base.

iv) Increasing order of boiling point.

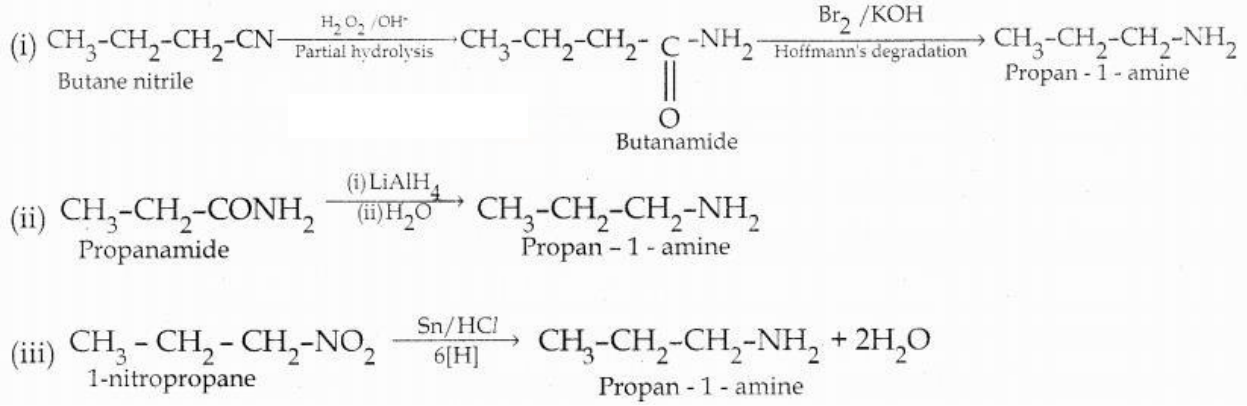
$(CH_3)_2NH < C_2H_5NH_2 < C_6H_5OH$
Hint > Amines generally have lower boiling point than alcohols of comparable molar mass. Since amines have weaker H-bonds.
Hint
Secondary amines
primary amines

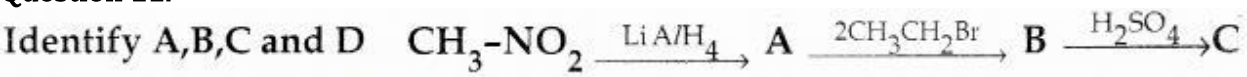
v) Decreasing order of pK values
$C_6H_5NHCH_3 > C_2H_5NH_2 > CH_3NH_2 > (C_2H_5)_2NH$
Hint > Basic character increases. pKb value decreases. Higher the basic nature, lower will be the pkb' value.

vi) Increasing order of basic strength
$C_6H_5NH_2 < C_6H_5\text{-}N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$
vii) Decreasing order of basic strength

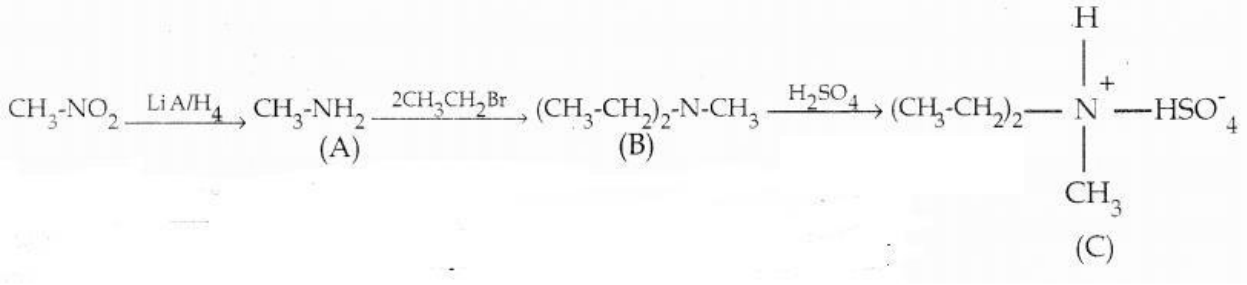


Question 10.
How will you prepare propan – 1 – amine from
Answer:
i) butane nitrile
ii) propanamide
iii) 1-nitropropane



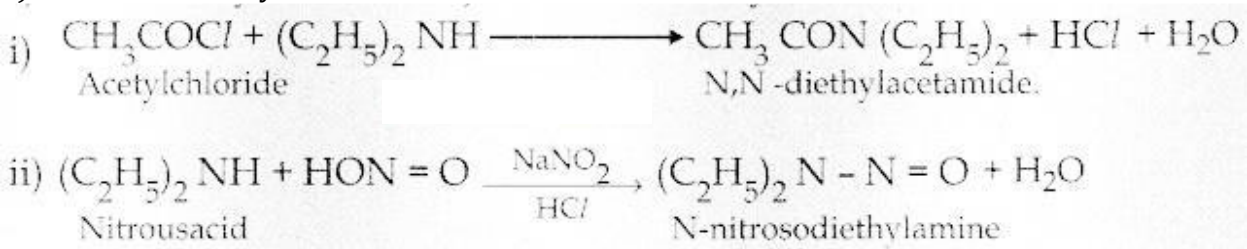
Question 11.
Identify A,B,C and D 

Answer:

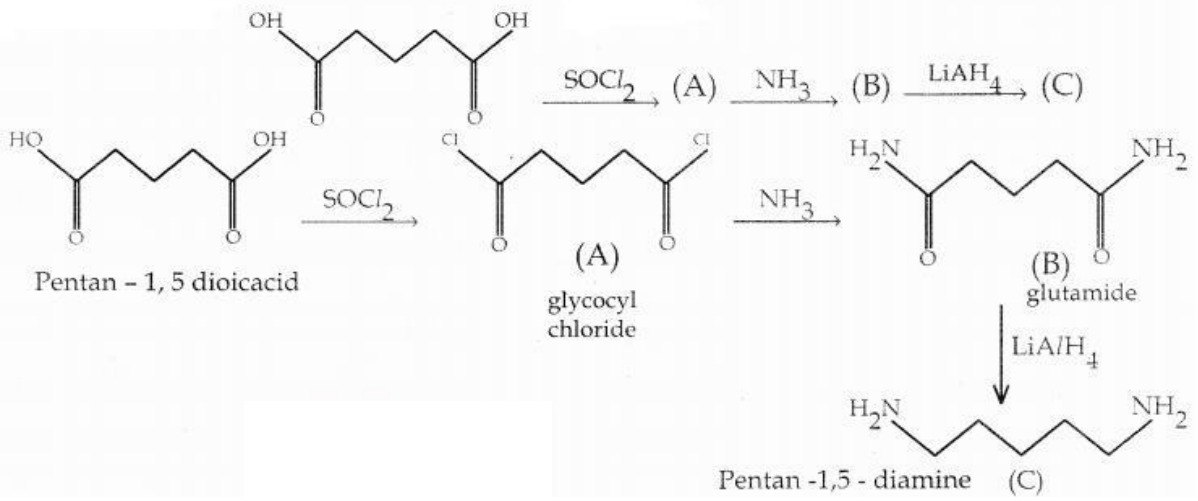


Compound	Name
A	Methanamirie
B	N – ethyl N – methyL ethanamine
C	Diethyl methyl ammonium hydrogen sulphate

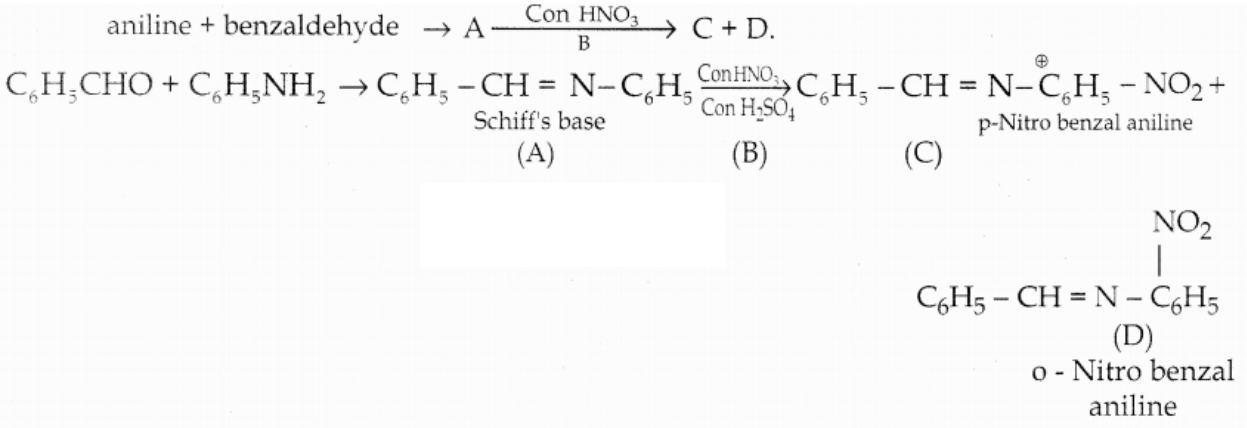
Question 12.
How will you convert diethylamine into
Answer:
i) N,N – dimethylacetamide
ii) N – nitrosódiethylamine



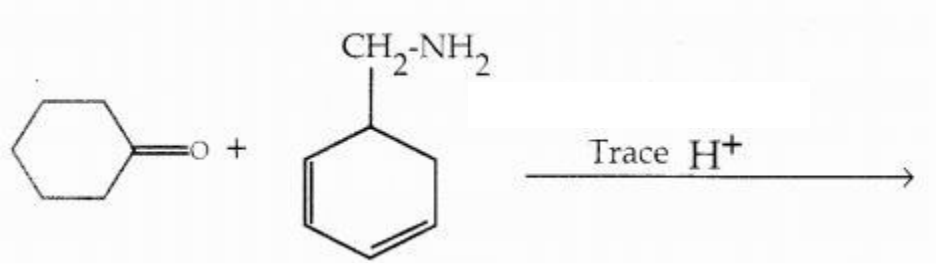
Question 13.
Identify A, B and C
Answer:



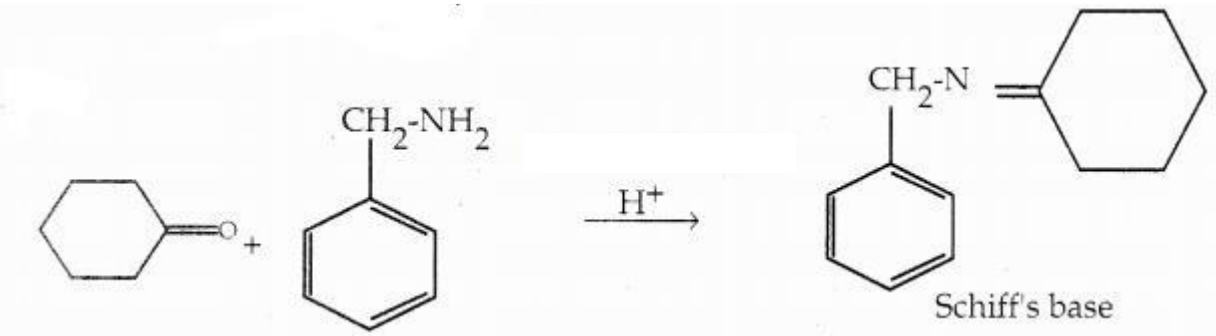
Question 14.
Identify A,B,C and D
Answer:



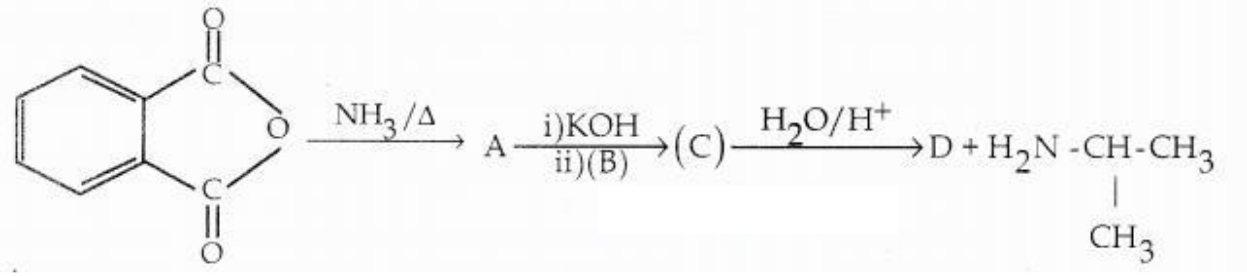
Question 15.
Complete the following reaction



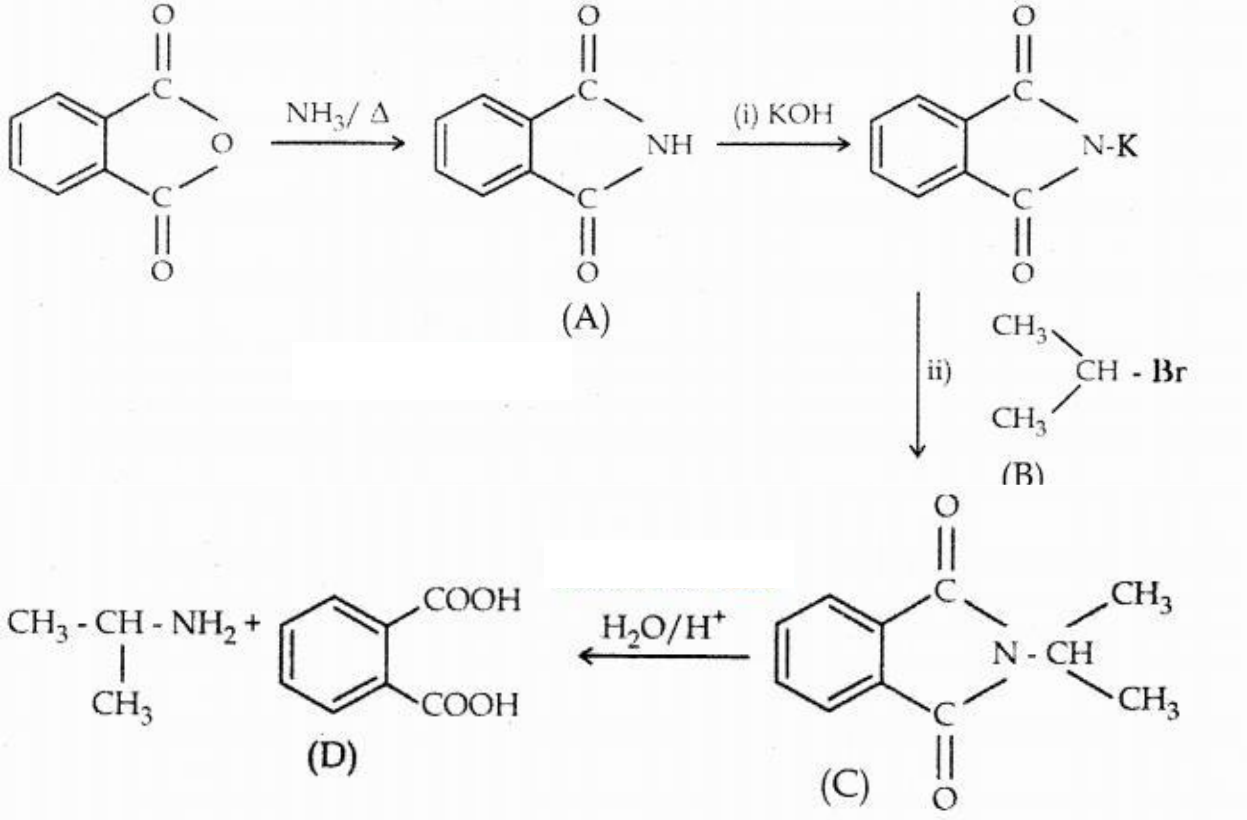
Answer:



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



Answer:



Compound	Name
A	Phthaliniide
B	Isopropyl bromide
C	N-isopropy1ththalimide
D	Phthalic acid

Question 17.

A dibromo derivative (A) on treatment with KCN followed by acid hydrolysis and heating gives a monobasic acid (B) along with liberation of CO_2 . (B) on heating with liquid ammonia followed by treating with Br_2 / KOH gives (c) which on treating with $NaNO_2$ and HC1 at low temperature followed by oxidation gives a monobasic acid (D) having molecular mass 74. Identify A to D.

Answer:

D is a monobasic and with molecular mass 74.

M.F of D is $CnH_{2n+1}COOH$

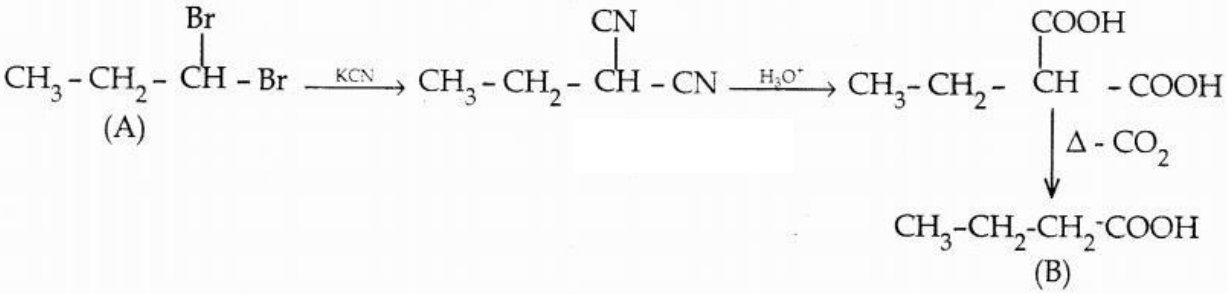
MolarMassis $12 \times n + 2n \times 1 + 1 \times 1 + 12 + 2 \times 16 + 1 \times 1 = 74$

$14n + 46 = 74$

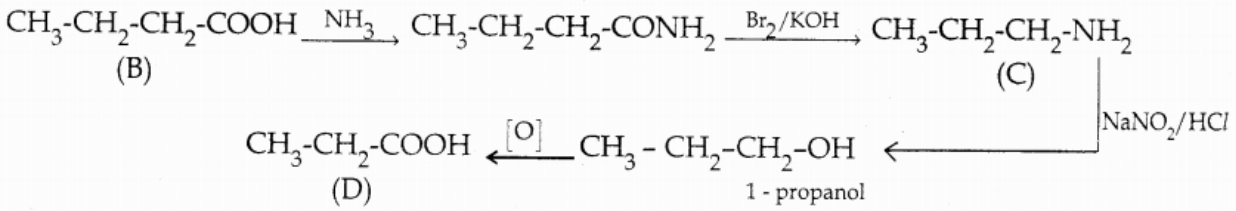
$14n=28$

$n=2$

∴ D is C_2H_5COOH ie CH_3-CH_2-COOH



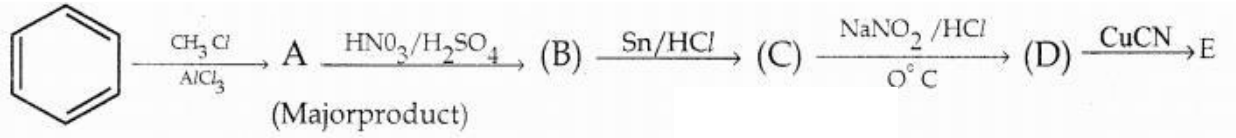
Hint : If two - COOH groups are present in the same carbon, on heating it loses CO_2 to form a monocarboxylic acid.



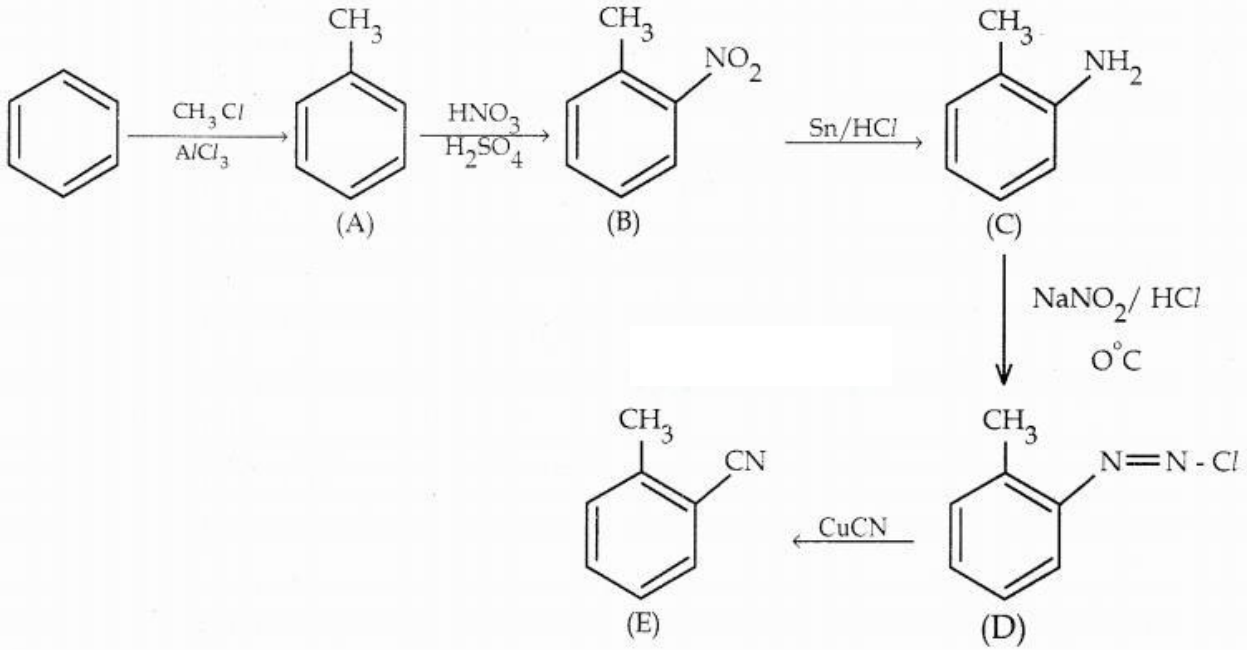
Compound	Name
A	1, 1- dibromopropane
B	Butanoic acid
C	1 – amino propane
D	Propanoic acid

Question 18.

Identify A to E in the following frequency of reactions



Answer:



Compound	Name
A	o – nitro toluene
B	o – amino toluene
C	o – amino toluene
D	o – methyl benzene diazonium chloride
E	o – cyano toluene