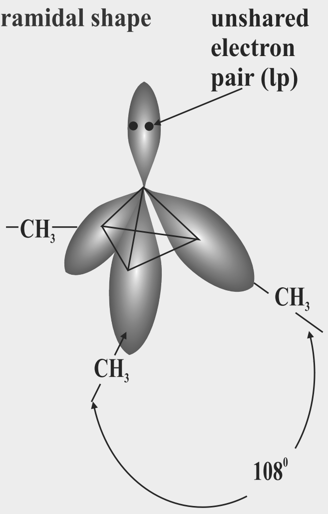
UNIT 13

AMINES

Points to Remember

Geometry

Pyramidal shape



Nomenclature

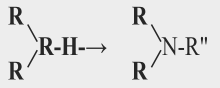
Common Names:- Amine is used as suffix after alkyl group e.g. $CH_3CH_2NH_2$ is ethylamine

IUPAC names:- e is replaced by - amine e.g. $CH_3CH_2NH_2$ is Ethanamine.

Classification and Nomenclature of Amines

Classification

$NH_3 \rightarrow RNH_2 \rightarrow$

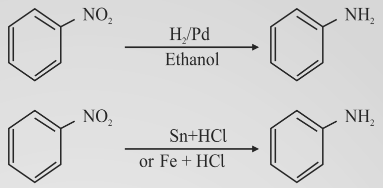


$$\begin{matrix}R\\R\end{matrix}\rangle R\text{-}H\text{-}\rightarrow \quad \begin{matrix}R\\R\end{matrix}\rangle N\text{-}R''$$

Primary(1^0) Primary(2^0) Primary(3^0)

Method of Preparation

1. Reduction of Nitro compounds



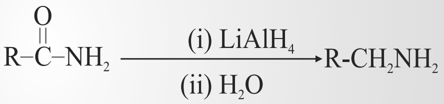
2. Ammonolysis Alkyl Halides

$$\ddot{N}H_3 + R\text{-}X \longrightarrow R\,\overset{+}{N}H_3\,X^-$$

3. Reduction of nitriles

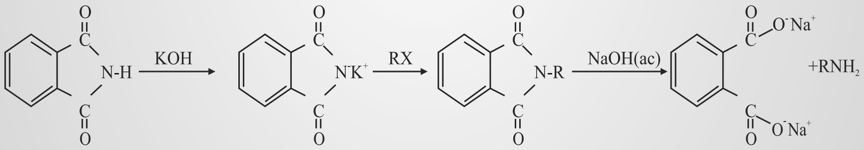
$$R-C\equiv N \xrightarrow[Na(Hg)/C_2H_3OH]{H_2/Ni} R\text{-}CH_2NH_2$$

4. Reduction of amide



$$R-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} R\text{-}CH_2NH_2$$

5. Gabriel phthalimide sythesis



6. Hoffmann bromamide degeneration reaction.

$$R-\overset{\overset{O}{||}}{C}-NH_2 + Br_2 + 4NaOH \longrightarrow R\text{-}NH_2 + Na_2CO_3 + 2NaBr + H_2O$$

Chemical Reactions:

(i) **Reactions Basic character:** Due to presence of lone pair of electrons on N of $-NH_2$ group they acts as base

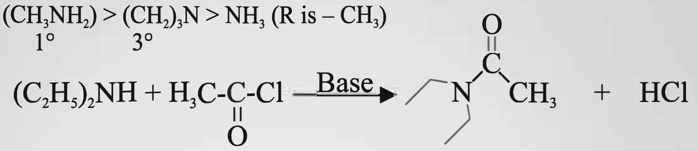
3° > 2° > 1° > ammonia (due to + 1 effect of alkyl group)

Basic Character in aqueous phase:

$\underset{2°}{(C_2H_5)_2NH} > \underset{3°}{(C_2H_5)_3N} > \underset{1°}{C_2N_5NH_2} > NH_3$ (R is other than $-CH_3$)

$\underset{2°}{(CH_3)_2NH} > \underset{1°}{(CH_3NH_2)} > \underset{3°}{(CH_2)_3N} > NH_3$ (R is $-CH_3$)

(ii) **Acylation**



(iii) **Carbylamine reaction:**

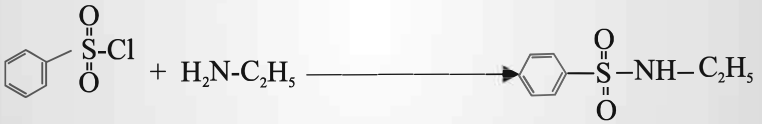
$$R\text{-}NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R\text{-}NC + 3KCl + 3H_2O$$

(iv) **With nitrous acid**

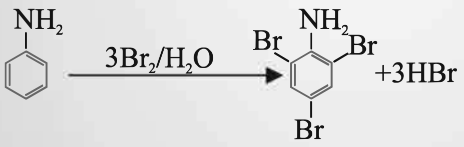
$$RNH_2 \xrightarrow{NaNO_2 + HCl} [R\text{-}\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

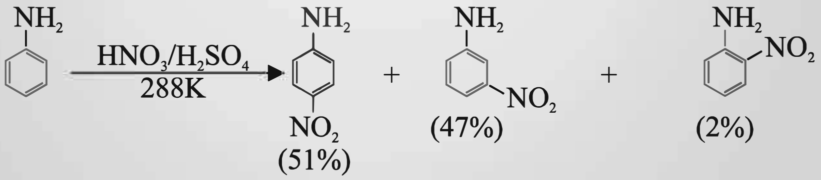
$$C_6H_5NH_2 \xrightarrow[273\text{-}278K]{NaNO_2 + HCl} C_6H_5\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$$

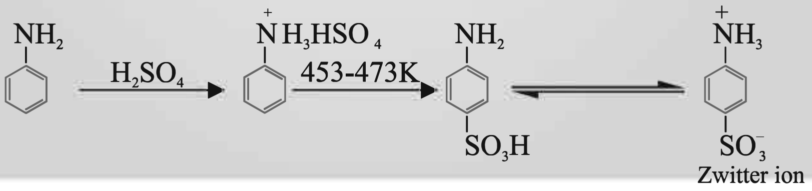
(v) **With Benzene sulphonyl chloride**



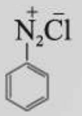
(vi) **Electrophilic Substitution**







Diazonium salt

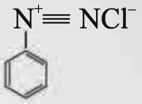


X^- may be Cl^-, Br^-, HSO_4^-, BF_4^-

Benzenedrazonium salt

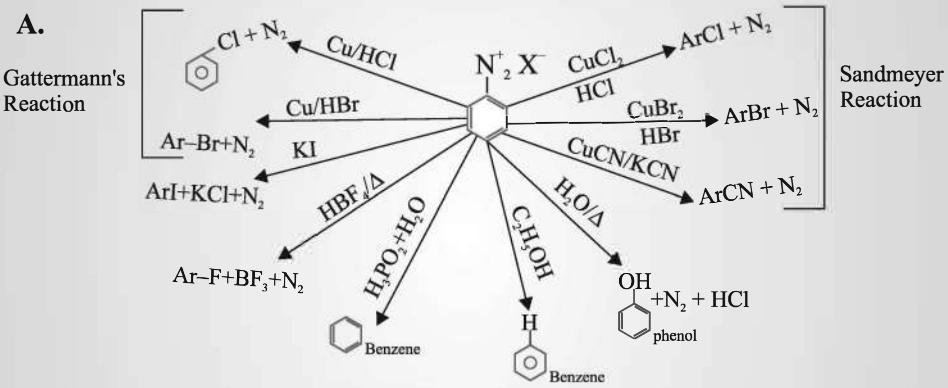
Preparation:

$$C_6H_5NH_2 + NaNO_2 + NCl \xrightarrow{0-5°C} C_6H_5\overset{+}{N}_2Cl^- + NaCl + H_2O$$

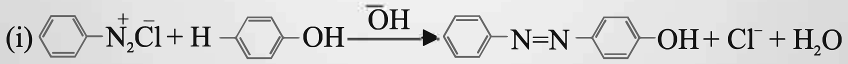


Reaction:

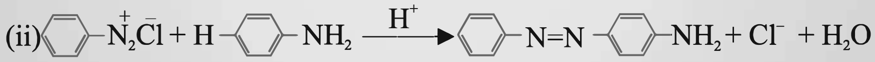
A.



B. Coupling Reaction



Orange dye
p-Hy*d*roxyazobenzene.



Yellow dye
(p-Aminozobenzene)

OBJECTIVE TYPE QUESTIONS

I MULTIPLE CHOICE QUESTIONS

1. In the nitration of benzene using conc. H_2SO_4 and conc. HNO_3 the species which initiates the reaction is:

(a) NO^+ (b) NO_2^+

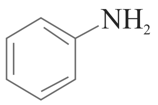
(c) NO_2^- (d) NO_3^-

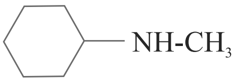
2. The correct IUPAC name of $CH_2=CH-CH_2NHCH_3$

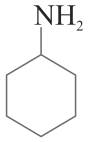
(a) Allylmethyl amine (b) 2-Aminopent-4-ene

(c) 4-Aminopent-l-ene (d) N-Methylprop-2-enamine

3. Which is the weakest base?

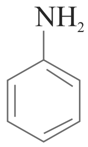
(a)


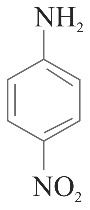
(b)


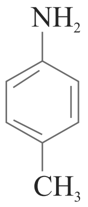
(c)


(d) H_3C-NH_2

4. The correct order of basic strength for the following compound is:

(i)


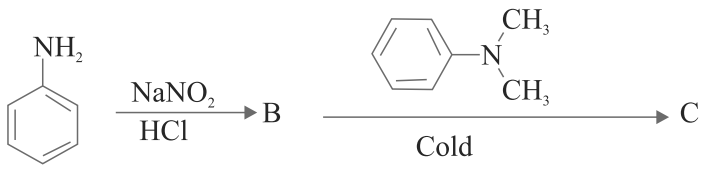
(ii)


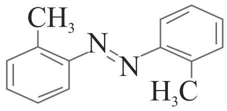
(iii)


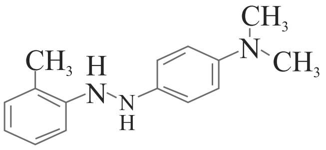
(a) ii < iii < i (b) iii < i < ii

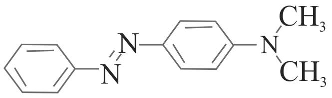
(c) iii < ii < i (d) ii < i < iii

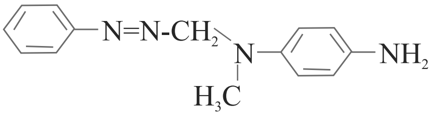
5. The structure of 'C' in following reaction sequence would be -



(a) 

(b) 

(c) 

(d) 

6. Which of the following statement about primary amine is false?

(a) Aryl amines react with nitrous acid to produce phenol

(b) Alkyl amines are stronger base than ammonia

(c) Alkyl amines are stronger base than aryl amines

(d) Alkyl amines react with nitrous acid to produce alcohol

7. Which of the following is most stable diazonium salt?

(a) $CH_3N_2^+X^-$ (b) $C_6H_5N_2^+X^-$

(c) $CH_3CH_2N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$

8. Method by which aniline can not be prepared is:

(a) Reduction of nitrobenzene with H_2/Pd in ethanol.

(b) Potassium salt of phthalimide treated with chlorobenzene

(c) Hydrolysis of phenyl isocyanide with acidic solution

(d) Degradation of benzamide with bromine in alkaline medium solution.

9. In the chemical reaction:

$CH_3CH_2NH_2 + CHCl_3 + 3KOH \rightarrow 'A' + 'B' + 3H_2O$

The compound 'A' and 'B' are respectively:

(a) $CH_3CH_2CONH_2$ and 3KCl

(b) CH_3CH_2NC and K_2CO_3

(c) CH_3CH_2NC and 3KCl

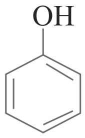
(d) CH_3CH_2CN and 3KCl

10. An amide (A) reacts with bromine in aqueous NaOH and forms amine containing three carbons. Identify (A):

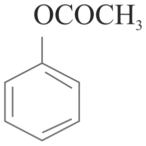
(a)	2- Methylpropanamide	(b)	Propanamine
(c)	Butanamide	(d)	None of these

11. Which of the following compound will give significant amount of *meta* product during mononitration reaction?

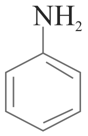
(a)



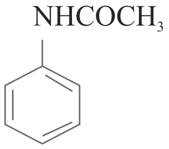
(b)



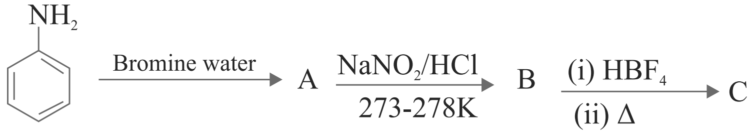
(c)



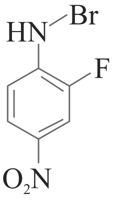
(d)



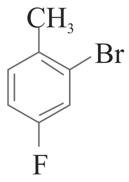
12. The final product C in the following sequence of reaction is:



(a)



(b)



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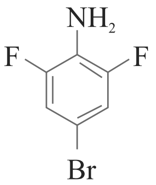
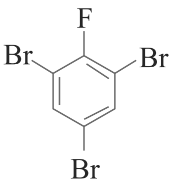
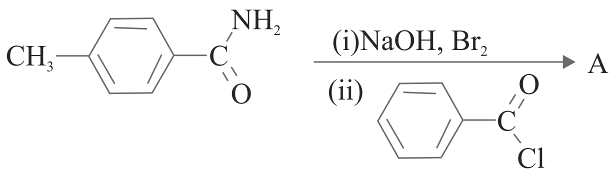
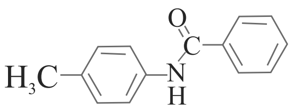


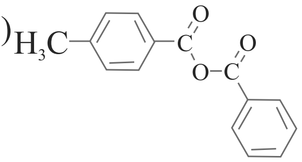
(d)



13. In the reaction, the structure of product A is:



(a)


(b)


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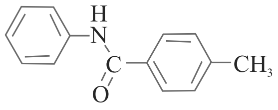
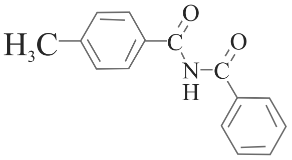
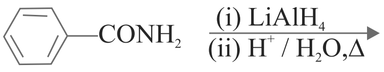


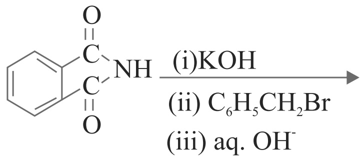
(d)


14. Which of the following reactions forms benzylamine?

(a)


(b) $C_6H_5CONH_2 \xrightarrow{NaOBr}$

(c) $C_6H_5CN \xrightarrow{H^+ / H_2O}$

(d)


15. Bromobenzene can be prepared from benzene diazonium chloride by its treatment with-

(a) Cu/HBr

(b) Br_2, hv

(c) CuBr/HBr

(d) Br_2/CCl_4

16. Acetamide and Ethylamine can be distinguish by reacting with

(a) aq. HCl and heat

(b) aq. NaOH and heat

(c) Acidified $KMnO_4$

(d) Bromine Water

17. The order of reactivity of halides with amines is
    (a) RI > RBr > RCl
    (b) RBr > RI> RCl
    (c) RCl > RBr > RI
    (d) RBr > RCl > RI
18. Which of the following does not affect the K_b of an organic base?
    (a) +I or -I effect
    (b) solvation effect
    (c) density
    (d) steric hinderance
19. Which of the following on reduction with $LiAlH_4$ yields a secondary amine?
    (a) Methyl isocyanide
    (b) Acetamide
    (c) Methyl cyanide
    (d) Nitroethane
20. In diazotisation of aniline with $NaNO_2$ and HCl acid the excess of acid is used primarily to
    (a) suppress the concentration of free aniline
    (b) suppress the hydrolysis to phenol
    (c) ensure a stoichlometric amount of HNO_2 acid
    (d) neutralise the base liberated.

II FILL IN THE BLANKS

1. Reaction of nitrobenzene with Fe + HCl results into the formation of...................
2. Aromatic amines are..............bases while aliphatic amines are..................bases than ammonia.
3. Gabriel phthalimide synthesis is used for synthesis of ....amines.
4. Benzenesulphonyl chloride is also known as..............reagent.
5. Butanamide on reaction with $LiAlH_4$ forms.................
6. To reduce activation of aniline it is deactivated by..................reaction.
7. Nitration of aniline forms *para* and .... isomers of nitroaniline as major products.
8. Benzene diazonium chloride may be converted into phenol by reaction with ....at 283 K.
9. Primary amines are soluble in water due to.............................

III ASSERTION REASON TYPE QUESTIONS

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Both assertion and reason are correct statements and reason is correct explanation of assertion.

(b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION** : Acylation of amines gives a monosubstituted product whereas alkylation of amines gives polysubstituted product.

   REASON : Acyl group sterically hinders the approach of further acyl groups.

2. **ASSERTION :** Hoffmann bromamide degradation reaction results into formation of primary amines.

   REASON : Primary amines are more basic than secondary amines.

3. **ASSERTION :** N-Ethylbenzenesulphonamide is soluble in alkali.

   REASON : Hydrogen attached to nitrogen in sulphonamide is strongly acidic.

4. **ASSERTION :** N, N-Diethylbenzenesulphonamide is insoluble in alkali.

   REASON : Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

5. **ASSERTION :** Only a small amount of HCl is required in the reduction of nitro compounds with iron scrap and HCl in the presence of steam.

   REASON : $FeCl_2$ formed gets hydrolysed to release HCl during the reaction.

6. **ASSERTION :** Aromatic 1° amines can not be prepared by Gabriel phthalimide synthesis.

   REASON : Aryl halides undergoes nucleophilic substitution with anion formed by phthalimide.

7. **ASSERTION :** Acetanilide is less basic than aniline.

   REASON : Acetylation of aniline results in decrease of electron density on nitrogen.

8. **ASSERTION:** n-Propylamine has higher boiling point than trimethylamine.

   REASON: Among n-Propylamine molecules, there is hydrogen bonding but there is not hydrogen bonding in trimethylamine.

9. **ASSERTION:** Aniline does not undergoes Friedel Crafts reaction.

   REASON: Friedel Crafts reaction is an electrophilic substitution reaction.

10. **ASSERTION:** Ethylamine is more basic than aniline.

    REASON: Due to +I effect of ethyl group electron density on nitrogen increases.

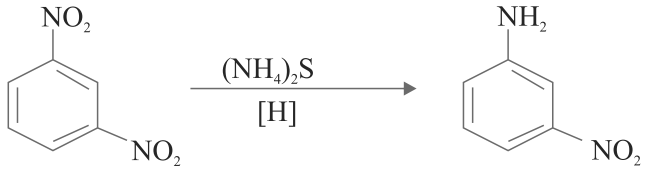
IV ONE WORD TYPE QUESTIONS

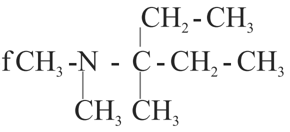
1. Name the reaction in which primary amines reacts with $CHCl_3$ and KOH forming foul smelling substance.
2. Write the IUPAC name of white precipitate formed by reaction of aniline with bromine water.
3. Write the product formed by the Hoffmann bromamide degradation of benzamide.
4. Is CH_3CONH_2 weaker or stronger base than $CH_3CH_2NH_2$?
5. Write the structure of reagent used to protect amino group in aniline.
6. Name the product formed when benzene diazonium chloride reacts with H_3PO_2.
7. Name the reaction which is used to convert diazonium salt into corresponding halide by reacting with Cu(I) halides.
8. Which type of reaction involves in the cleavage of C-X bond in ammonolysis ?
9. What is the pH during coupling reaction between phenol and benzendiazonium salt.
10. Write the reagent which can be used to convert nitrobenzene to aniline
11. How many structural isomer are possible for $C_4H_{11}N$ compound?
12. Name the reagent for the conversion of amide to amine containing same number of carbon atom.
13. What kind of substitution involved in Gabriel phthalimide systhesis?
14. Name the solvent which we used in acetylation of aniline using acetic anhydride.

VERY SHORT ANSWER TYPE QUESTIONS (1 Marks)

1. Convert *m*-dinitrobenzene to m-nitroaniline.

Ans.



2. Write IUPAC name of 

$$CH_3-\underset{\substack{|\\CH_3}}{N}-\overset{\substack{CH_2-CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_2-CH_3$$

Ans. 3-Methyl-N,N-dimethylpentanamine

3. Give one use of quaternary ammonium salts.

Ans. It is used as detergents, e.g., $[CH_3(CH_2)_{15}N(CH_3)_2]^+Cl^-$

4. Mention the chemical formula of Hinsberg's reagent.

Ans. Benzene sulphonyl chloride, $C_6H_5-SO_2Cl$

5. Why aniline dissolves in HCl?

Ans. $C_6H_5NH_2 + HCl \rightarrow [C_6H_5NH_3]^+Cl^-$

It dissolves due to its basic nature.

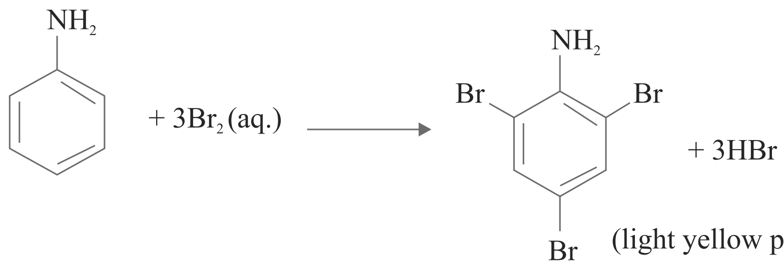
6. How will you test the presence of primary amine?

Ans. By carbylaminc test.

$RNH_2 + CHCl_3 + 3KOH \rightarrow R\text{-}NC + 3H_2O$

7. What happens when aniline is treated with bromine?

Ans.



(light yellow ppt.)

8. Write a chemical equation to illustrate the ammonolysis.

Ans. For alcohols:

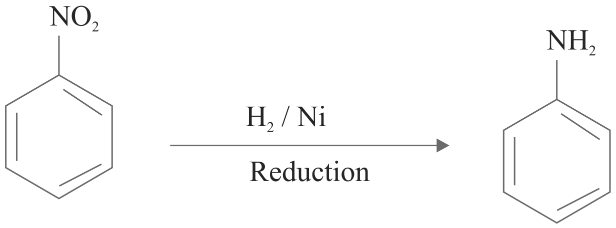
$$C_2H_5OH \xrightarrow[Al_2O_3\ /\ 620K]{NH_3} C_2H_5NH_2 \xrightarrow[-H_2O]{C_2H_5OH} (C_2H_5)_2NH \xrightarrow{C_2H_5OH} (C_2H_5)_3N$$

For alkyl halides:

$$C_2H_5I \xrightarrow[-HI]{NH_3\ /\ 373K} C_2H_5NH_2 \xrightarrow[-HI]{C_2H_5I} C_2H_5)_2NH_2 \xrightarrow[-HI]{C_2H_5I} (C_2H_5)_3N \xrightarrow[-HI]{C_2H_5I} [(C_2H_5)_4N]^+I^-$$

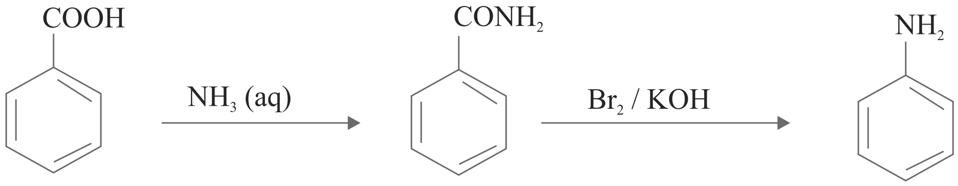
9. Convert nitrobenzene into aniline.

Ans.



10. Convert C_6H_5COOH to $C_6H_5NH_2$

Ans.



11. Write the name of isomerism exhibited by different amines.

Ans. Chain, position, metamerism, functional.

12. Arrange the following compounds in increasing order of solubility in water:

$C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$

13. What is the role of HNO_3 in the nitrating mixture used for nitration of benzene.

Ans. HNO_3 provides NO_2^+ electrophile.

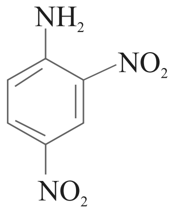
14. Why $C_6H_5\overset{+}{N_2}\overset{-}{Cl}$ not stored and is used immediately after its preparation?

Ans. It is highly unstable

15. What is the best reagent to convert $C_6H_5CONH_2$ into aniline?

Ans. $Br_2 + NaOH$

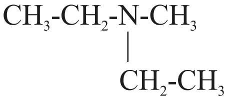
16. Write of IUPAC of



Ans. 2,4-Dinitrobenzamine/2,4 Dinitroaniline

17. Write the structure of N-Ethyl-N-methyl ethanamine

Ans.



$CH_3\text{-}CH_2\text{-}\underset{\underset{CH_2\text{-}CH_3}{|}}{N}\text{-}CH_3$

18. Rearrange the following compound in an increasing order of their basic strength.
Aniline, p-nitroaniline, P- toluidine.

Ans. p-Nitroaniline< Aniline<p-Toluidine

19. Ammonolysis of alkyl halide does not give amine in pure state why.

Ans. Because 2° and 3°, amines are also formed

20. A poisonous gas is formed by the reaction of R-NH_2 with $CHCl_3$, KOH. Give the name of the test.

Ans. Carbylamine test

21. Out of Pentan-1-ol and pent-1-amine,which is more soluble?

Ans. pentan-1-ol

22. Identify A and B:

$$CH_3COO\,C_2H_5 \xrightarrow{NH_3} A \xrightarrow{Br_2/KOH} B$$

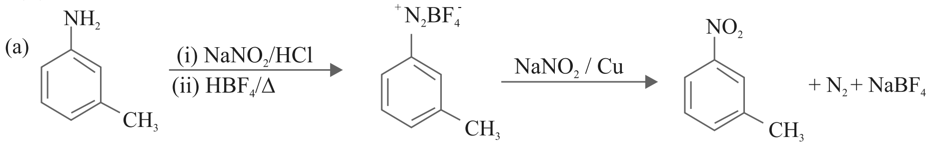
Ans. A- CH_3-$CONH_2$ B- CH_3-NH_2

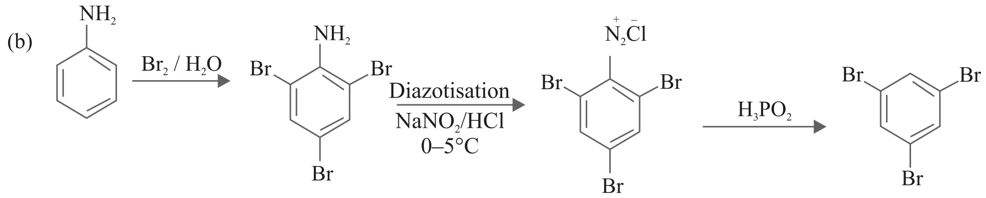
23. Write the name of test to distinguish between ethanamine and N-ethyl ethananine

Ans. Hinsberg Test.

SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. How will you convert following :
   (a) 3-Methlylaniline to 3-Nitrotoluene
   (b) Aniline to 1,3,5-Tribromobenzene





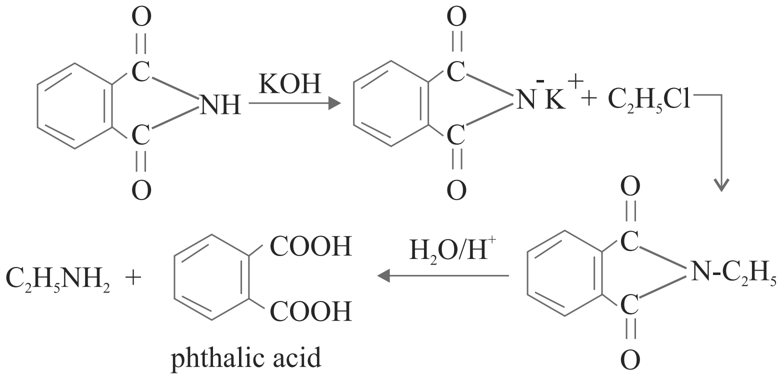
2. A compound 'A' having molecular formula C_3H_7ON reacts with Br_2 in presence of NaOH to give compound. 'B' This compound 'B' reacts with HNO_2 to form alcohol and N_2 gas. Identify compound 'A' and 'B' and write the reactions involved.

$$\underset{(A)}{CH_3CH_2CONH_2} \xrightarrow[NaOH]{Br_2} CH_3CH_2NH_2 \xrightarrow{HNO_2} \underset{(B)}{C_2H_5OH + N_2 + H_2}$$

3. Account for following:
   (i) Amino group in aniline is *o*- and *p*- directing in aromatic electrophilic substitution reactions but aniline on nitration gives a substantial amount of *m*-nitroaniline.
   (ii) Aniline does not undergoes Friedel Crafts reaction.

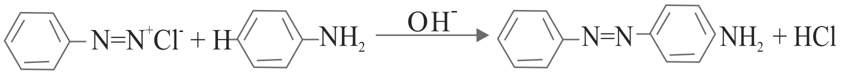
Ans. (i) It is because aniline is protonated to form anilinium cation, in which $-NH_3^+$ group is *meta*-directing.
   (ii) It is because aniline is Lewis base can form adduct with $AlCl_3$ which deactivates the ring.

4. How will you synthesise ethanamine by Gabriel phthalimide synthesis?



5. Write short notes on following:
   (a) Coupling reaction
   (b) Ammonolysis

Ans : (a)



Ammonolysis : $\mathrm{R\text{-}X + NH_3 \rightarrow R\text{-}NH_2 + HX}$

$\mathrm{RNH_2 + R\text{-}X \rightarrow (R)_2NH + HX}$

$\mathrm{(R)_2NH + R\text{-}X \rightarrow (R)_3N + HX}$

$\mathrm{(R)_3N + R\text{-}X \rightarrow [R_4N^+]X^-}$

6. Account for the following :

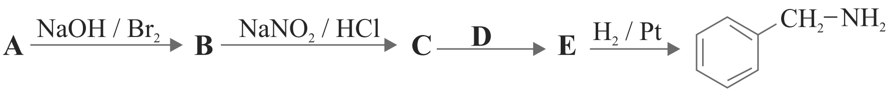
(b) (a) Electrophilic substitution in aromatic amines takes place more readily than benzene.

(b) Nitro compounds have higher boiling points than hydrocarbons having almost same molecular mass.

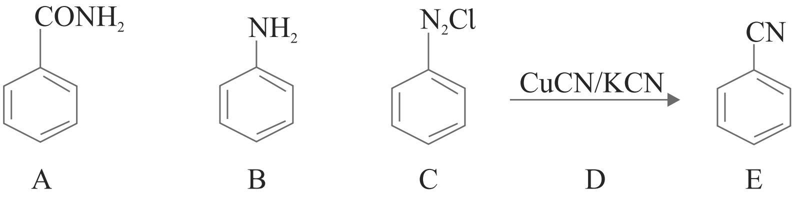
Ans. (a) - $\mathrm{NH_2}$ is electron releasing group so electrophilic substitution takes place faster.

(b) Nitro compounds are more polar than hydrocarbons therefore have Stronger vander Waals forces.

7. Write the structure of reagents/organic compounds 'A' to 'E' :



Ans :



8. What happens when :

(a) An alkyl halide reacts with $\mathrm{AgNO_2}$ and product is reduced.

(b) An alkyl halide is treated with AgCN and product is hydrolysed.

(c) Methyl magnesium bromide is treated with cyanogen chloride.

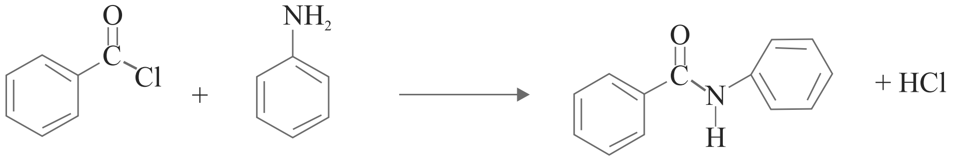
Ans. (a) $\mathrm{R\text{-}X + AgNO_2 \xrightarrow[-AgX]{} R\text{-}NO_2 \xrightarrow[{[H]}]{Sn/HCl} R\text{-}NH_2}$

(b) $\mathrm{R\text{-}X + AgCN \xrightarrow[-AgX]{} RNC \xrightarrow{H_2O/H^+} RNH_2 + HCOOH}$

(c) $\mathrm{CH_3MgBr + CN\text{-}Cl \rightarrow CH_3CN + Mg<^{Cl}_{Br}}$

9. Write reaction for benzoylation of aniline.

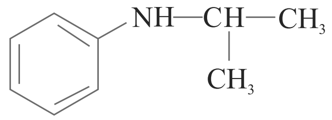
Ans :



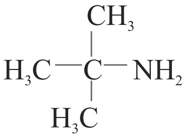
N-phenyl benzamide

10. Draw structure of the following compounds:
   (a) N-Isopropylaniline
   (b) t-Butylamine

Ans : (a)



(b)

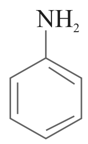


$$H_3C-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large H_3C}{|}}{C}}-NH_2$$

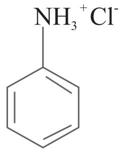
11. Give reasons:
   (a) Electrophilic substitution in aromatic amines takes place more readily than benzene.
   (b) Ethylamine and acetamide both contain amino group but acetamide does not show basic nature.

Ans: (a) -NH$_2$ group in aromatic amines shows +R effect and increases electron density on ring and facilitating the attack of electrophile.
   (b) In acetamide the electron pair on nitrogen is in resonance with carbonyl group so electrons are less readily available than ethylamine.

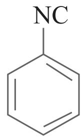
12. An organic aromatic compound 'A' with the molecular formula C_6H_7N is sparingly soluble in water. 'A' on treatment with dil. HCl gives a water soluble compound 'B'. 'A' also reacts with chloroform in presence of alcoholic KOH to form an obnoxious smelling compound 'C'. 'A' reacts with benzene sulphonyl chloride to form alkali soluble compound 'D'. 'A' reacts with $NaNO_2$ and HCl to form a compound `E' which on reaction with phenol forms an orange dye. Elucidate the structures of the organic compounds from 'A' to 'F'.



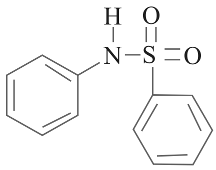
A



B

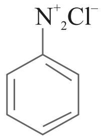


C

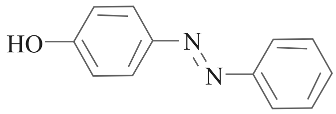


D

E



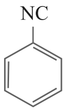
F



13 Write chemical distinguish test between following pair of compound.

(i) Aniline and N-Methylaniline

(ii) $(CH_3)_2$ NH and $(CH_3)_3N$

Ans. (i) Aniline + $CHCl_3$+KOH →  Foul smell

N-Methyl aniline + $CHCl_3$ + KOH → No reaction

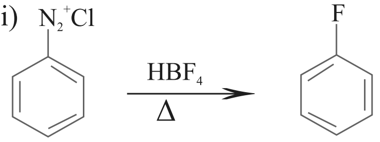
(ii) $(CH_3)_2$ NH+HNO_2 Yellow oily compound

$(CH_3)_3N$ + HNO_2 Salt soluble in water

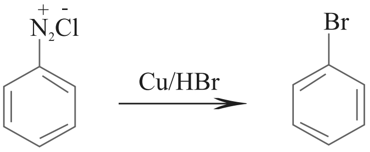
14. Write the main product when benzene dyazonium salt reacts with following reagent

(i) HBF_4/Δ (ii) Cu/HBr (iii) H_2O

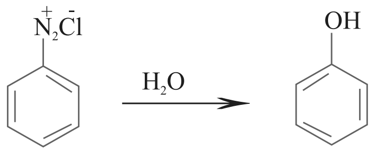
Ans. (i)



(ii)



(iii)

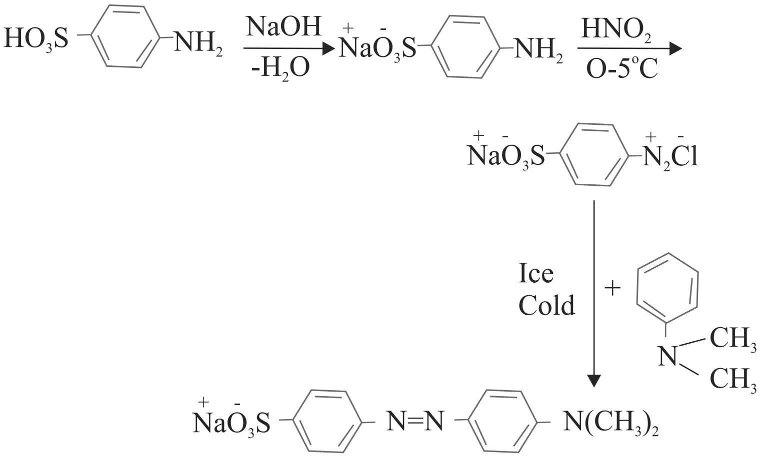


15. Write the method to prepare a pure sample of primary amine having one more carbon than the alkyl halide used ?

Ans. $R\text{-}X \xrightarrow{KCN\ (Alc)} R\text{-}CN \xrightarrow[(Reduction)]{LiAlH_4} R\text{-}CH_2\text{-}NH_2$

16. How will you prepare methyl orange from sulphanilic acid ?

Ans.



Methyl Orange

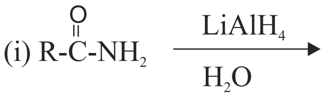
17. Why methylamine in water react with ferric chloride to precipitate hydrated ferric oxide.

Ans: Methylamine form soluble hydroxide in reacting with water the $\overline{O}H$ ion released combine with Fe^{3+} ion to give forric hydroxide.

$CH_3NH_2 + H_2O \longrightarrow CH_3\text{-}\overset{+}{N}H_3 + \overline{O}H$

$2Fe^{3+} + 6OH^- \longrightarrow 2Fe(OH)_3$ or $Fe_2O_3.3H_2O$

18. Complete the following reactions:



(i) $R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \xrightarrow[H_2O]{LiAlH_4}$

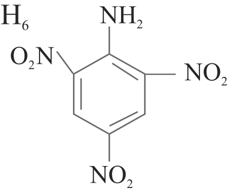
(ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

(iii) $C_6H_5\ NH_2 + \text{Conc. } HNO_3 \longrightarrow$

Ans. (i) $R\text{-}CH_2\text{-}NH_2$

(ii) C_6H_6

(iii)



19. Give reason why trimethylamine reacts with BF_3 while triphenylamine does not.

Ans: In trimethylaniline $(Me)_3N$, the methyl group show +I effect , hence increase the reactivity towards Lewis acid (BF_3). While in (Ph_3N, Phenyls group (C_6H_5) show -I effect which decrease the e^- density over N atom. hence reactivity decreases towards Lewis acid (BF_3)

20. Why is *para* nitroaniline is weaker base than **m-nitroaniline**?

Ans. Because Nitro group at para position exhibits a strong electron withdrawing effect dut to –R and –I effects and hence decreases electron density from $-NH_2$ as compared to nitro group at m-position, where it only exhibits –I effect.

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Arrange the following :
   - (a) In decreasing order of pK_b value
     $C_2H_5NH_2, C_6H_5NHCH_3, (C_2H_5)_2NH$ and $C_6H_5NH_2$
   - (b) In increasing order of basic strength:
   - (i) Aniline , *p*-Nitroaniline and *p*- Toluidine
   - (ii) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$
   - (c) In decreasing order of basic strength :
     $C_6H_5NH_2$, $(CH_3)_2NH$, CH_3NH_2
   - (d) Decreasing order of basic strength in gas phase :
     $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, NH_3
   - (e) Increasing order of boiling point :
     C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$

Ans : (a) $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

(b) (i) *p*- Nitroaniline < Aniline < *p* -Toluidine

(ii) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

(c) $(CH_3)_2NH_2 > CH_3NH_2 > C_6H_5NH_2$

(d) $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$

(e) $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$

2. How will you convert the following compound:
   - (i) Ethanoic acid into Methanamine
   - (ii) Hexanenitrile into 1- Aminopentane
   - (iii) Nitromethane to Dimethylamine
   - (iv) Ethanamine into Methanamine

Ans. (i) $\underset{\text{Methanol}}{CH_3COOH} \xrightarrow{NH_3} CH_3CONH_2 \xrightarrow[NaOH]{Br_2} CH_3NH_2$

(ii) $\underset{\text{Hexane nitrile}}{CH_3(CH_2)_4CN} \xrightarrow[\text{partial hydrolysis}]{\text{Conc. HCl}} \underset{\text{Hexanamide}}{CH_3(CH_2)_4CONH_2} \xrightarrow{Br_2 / KOH} \underset{\text{1-Aminopentane}}{CH_3(CH_2)_4NH_2}$

(iii) $\underset{\text{Methanol}}{CH_3NO_2} \xrightarrow{H_2/Ni} CH_3NH_2 \xrightarrow{CHCl_3/KOH} CH_3NC \xrightarrow{H_2/Ni} \underset{\text{Ethanoic acid}}{CH_3NH–CH_3}$

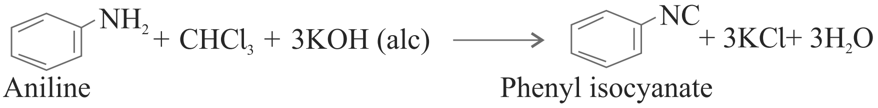
(iv) $\underset{\text{Ethanamine}}{CH_3CH_2NH_2} \xrightarrow[(NaNO_2 + HCl)]{HNO_2} CH_3CH_2OH \xrightarrow{KMnO_4/H^+} CH_3COOH \xrightarrow{aq.\ NH_3} CH_3COONH_4$

$\xrightarrow{\text{heat}} CH_3CONH_2 \xrightarrow{Br_2/KOH} \underset{\text{Methanamine}}{CH_3NH_2}$

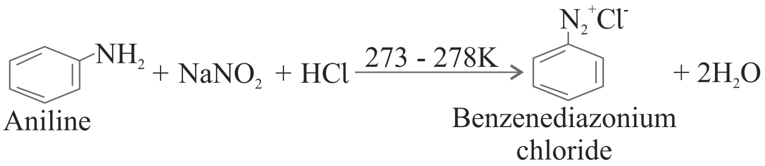
3. Write short note on the following :-
   (a) Carbylamine reaction
   (b) Diazotization
   (c) Hoffmann bromamide degradation reaction
   (d) Coupling reaction
   (e) Ammonolysis

(i) **Carbylamine reaction** : When primary amine (aromatic or aliphatic) warmed with chloroform and alc. KOH, isocyanides are formed which can be identified by their offensive smell. This test is used to identity the presence of primary amine or chloroform.

$$RCH_2NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow RCH_2NC + 3KCl + 3H_2O$$



(b) **Diazotization** : When primary aromatic amine is treated with $NaNO_2$ and HCl at 273-278K, diazonium salt is obtained. This reaction is known as diazotization.



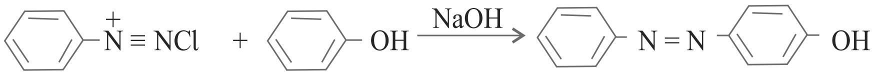
Benzenediazonium chloride is a very important synthetic compound, which can be changed into haloarenes, phenol, cyanobenzene, benzene etc.

(c) **Hoffmann bromamide degradation reaction** : When any primary amide (aliphatic or aromatic) is treated with bromine and alkali, it gives the amine with one less carbon atom.

$$R-\overset{\overset{\displaystyle O}{||}}{C}-NH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + K_2CO_3 + 2KBr + 2H_2O$$

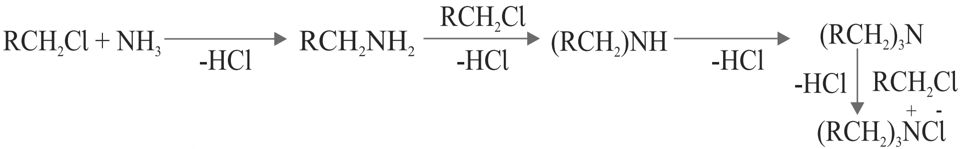
This reaction is used to reduce one carbon atom form a compound.

(d) **Coupling reaction** : When benzenediazonium chloride is treated with phenols or aromatic amines, azo dyes arc produced in which diazo (- N = N -) group is retained. Coupling reactions generally take place at *p*-position of phenol or aromatic amines.



Benzendiazonium chloride Phenol *p*-Hydroxyazobeneze (Azo dye)

(e) **Ammonolysis** : Reaction of alkyl halides with ammonia is known as ammonolysis. Ammonolysis generally gives the mixture of 1°, 2°, 3° amines and quaternary ammonium salt.



$$RCH_2Cl + NH_3 \xrightarrow[-HCl]{} RCH_2NH_2 \xrightarrow[-HCl]{RCH_2Cl} (RCH_2)NH \xrightarrow[-HCl]{} (RCH_2)_3N \xrightarrow[-HCl]{RCH_2Cl} (RCH_2)_3\overset{+}{N}\overset{-}{Cl}$$

4. Complete the following reaction :-

(i) $C_6H_5NH_2 + H_2SO_4$(conc.) →

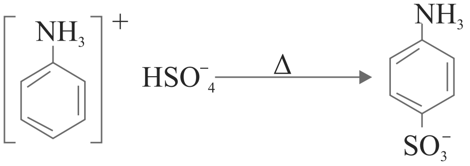
(ii) $C_6H_5N_2Cl + C_2H_5OH$ →

(iii) $C_6H_5NH_2 + (CH_3CO)_2O$ →

(iv) $C_6H_5N_2Cl + H_3PO_2 + H_2O$ →

(v) $C_6H_5NH_2 + CHCl_3 + 3KOH$ (alc.) →

Ans: (i)



(ii) $C_6H_6 + N_2 + HCl + CH_3CHO$

(iii) $C_6H_5NHCOCH_3 + .CH_3COOH$

(iv) $C_6H_6 + H_3PO_3 + HCl + N_2$

(v) $C_6H_5NC + 3KCl + 3H_2O$

5. Accomplish the following conversion :-

(i) $C_6H_5NO_2 \rightarrow C_6H_5\,COOH$

(ii) Benzene → *m*-Bromophenol

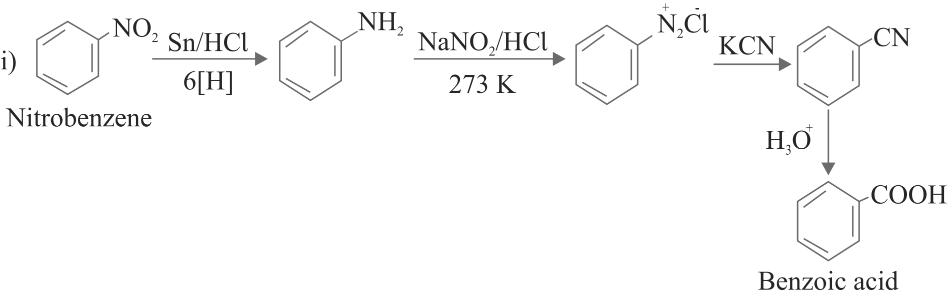
(iii) $C_6H_6COOH \rightarrow C_6H_5NH_2$

(iv) Aniline → 2,4,6 -Tribromoaniline

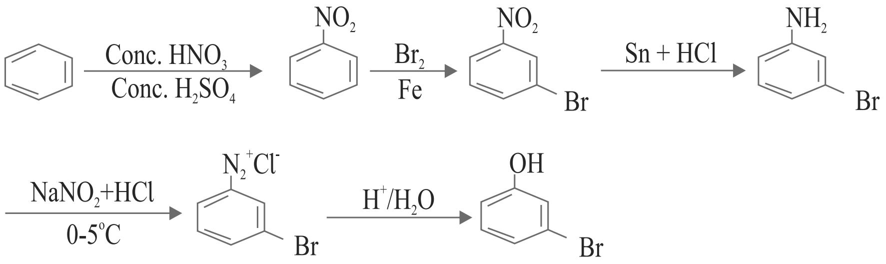
(v) Benzylchloride → 2-Phenylethanamine

Ans:-

(i)



(ii)



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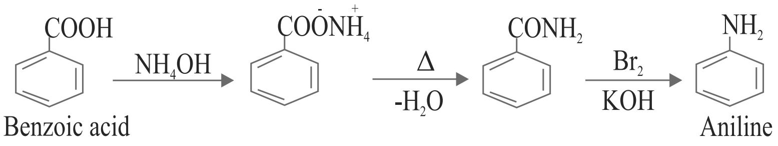

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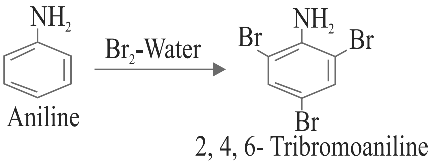
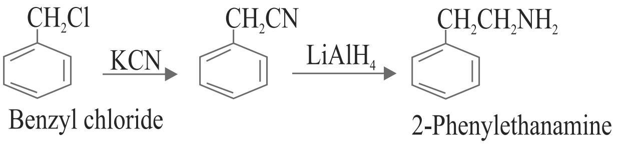


(v)



7. Write A,B and C in the given reaction sequences;

(i) $C_6H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{NH_3} C$

(ii) $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$

(iii) $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow[273K]{HNO_2} B \xrightarrow[\Delta]{H_2O/H_+} C$

(iv) $CH_3COOH \xrightarrow[\Delta]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C$

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

Ans. (i) C_6H_5CN, C_6H_5COOH, $C_6H_5CONH_2$

(ii) CH_3CH_2CN, $CH_3CH_2CH_2NH_2$, $CH_3CH_2CH_2OH$

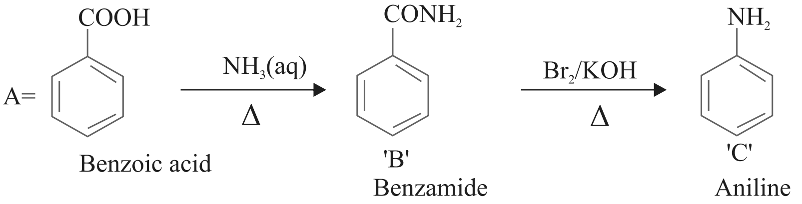
(iii) $C_6H_5NH_2$, $C_6H_5\overset{+}{N_2}\overset{-}{Cl}$, C_6H_5OH

(iv) CH_3CONH_2, CH_3NH_2, CH_3OH

(v) CH_3CH_2CN, $CH_3CH_2\text{-}CO\text{-}NH_2$, $CH_3\text{-}CH_2\text{-}NH_2$

8. An organic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structure and IUPAC of compound A, B and C.

Ans.



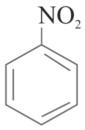
9. Write the structure of compound **A** to **E** in the following sequence of reaction. E is N-methyaniline

$$[A] \xrightarrow[H_2SO_4]{HNO_3} [B] \xrightarrow[\Delta]{Sn/HCl} [C] \xrightarrow[KOH/\Delta]{CHCl_3} [D] \xrightarrow{H_2/Pt} [E]$$

Ans. A=

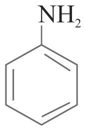
Benzene

B=



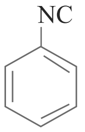
Nitrobenzene

C=



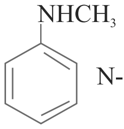
Aniline

D=



Phenylisocyanide

E=



N-methylaniline

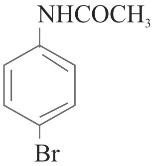
10. Write the structure A, B, C, D, E in the given reaction.

$$\begin{tikzcd}
C_6H_5NH_2 \arrow[r, "CH_3COCl", "Pyridine"'] \arrow[d, "CHCl_3+KOH"] & {[A]} \arrow[r, "Br_2/CH_3COOH", "\Delta"'] \arrow[d, "HNO_3+H_2SO_4"] & {[B]} \arrow[r, "O\bar{H}/H^+"] & {[C]} \\
D & E & &
\end{tikzcd}$$

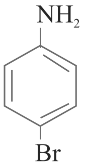
Ans.

A= $C_6H_5NHCOCH_3$

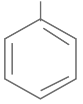
B=



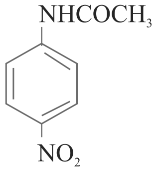
C=



D=



E=



CASE-STUDY BASED QUESTIONS

1. **Read the passage and answer the following questions:**

Friedel-Crafts (FC) reaction is an important method to incorporate carbon skeletons into aromatic system. Great successes have been achieved for the hydroarylation of neutral arenes (such as toluene, anisole, and their homologues). Because the FC reactions typically require Lewis acid catalysts, for arenes containing nitrogen atom, the substrate scope of FC reactions are quite limited due to the coordination between amine and Lewis acid catalyst, except indole and pyrrole. Being profited from the extremely weak basic properties, acid-catalyzed additions of indole and pyrrole to alkenes have obtained great achievements. However, the hydroarylation of alkaline arenes to alkenes still remains many challenges. Some researches have shown the possibility of hydroarylation between the parent anilines $C_6H_5NH_2$ and alkenes. However, the reaction of arenes with stronger basicity (such as N,N-dimethylaniline and N,N-diethylaniline) still is a big problem, due to their ability to coordinate with Lewis acid catalyst which can lead to deactivation of the aromatic ring. Furthermore, alkaline arenes can trap the proton in the C-H activation process and the reaction will be terminated as result.

Recently, Bertrand et al. reported an anti-Bredt cyclic diaminocarbene which showed increased λ-accepting character without diminishing its cs-donor property. We found that Gold(I) compound derived from this new carbene can be used as effective catalyst for the FC reaction between alkenes and N,N-dialkylanilines. Now, these new FC reactions are receiving more and more research interests. As we known, most of the electrophilic substitution reactions followed the Markovnikov rule. For the FC reaction of alkenes, the reactions following the Markovnikov rule should form branched product. Only several examples were reported on the formation of linear product by anti-Markovnikov rule. For the FC reactions between alkenes and N, N-dialkylanilines catalyzed by carbene Gold(I), both Markovnikov and anti-Markovnikov hydroarylations were observed and all these reactions gave high para-selectivity products. The selectivity to the branched or linear product was highly depended on the structure of alkenes.

Reference : Wu, H., Zhao, T. & Hu, X. **Friedel-Crafts Reaction of N,N-Dimethylaniline with Alkenes** *Catalyzed by Cyclic Diaminocarbene-Gold(I) Complex*. *Sci Rep* 8, 11449 (2018). https://doi.org/10.1038/s41598-018-29854-0

(A) Why aniline does not undergoes Friedel-Crafts reaction?

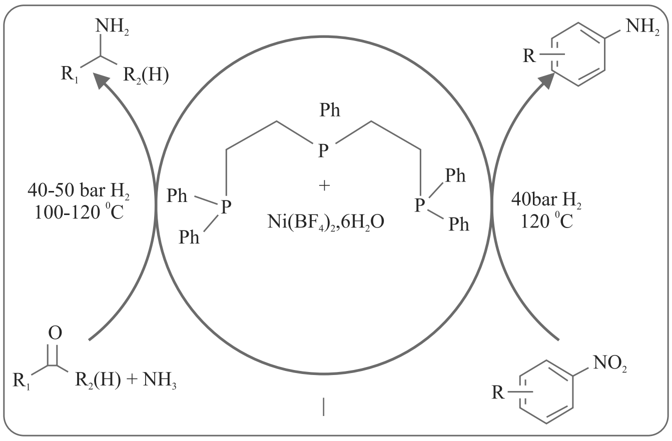
(B) Write reaction to convert aniline into N,N-dimethylaniline.

(C) How *p*- Nitroaniline can be synthesised from Aniline?

(D) Why -NH_2 group in aniline is *ortho-* , *para-* directing?

2. **Read the passage and answer the following questions:**

The development of base metal catalysts for industrially relevant amination and hydrogenation reactions by applying abundant and atom economical reagents continues to be important for the cost-effective and sustainable synthesis of amines which represent highly essential chemicals. In particular, the synthesis of primary amines is of central importance because these compounds serve as key precursors and central intermediates to produce value-added fine and bulk chemicals as well as pharmaceuticals, agrochemicals and materials. Here we report a Ni-triphos complex as the first Ni-based homogeneous catalyst for both reductive amination of carbonyl compounds with ammonia and hydrogenation of nitroarenes to prepare all kinds of primary amines. Remarkably, this Ni-complex enabled the synthesis of functionalized and structurally diverse benzylic, heterocyclic and aliphatic linear and branched primary amines as well as aromatic primary amines starting from inexpensive and easily accessible carbonyl compounds (aldehydes and ketones) and nitroarenes using ammonia and molecular hydrogen. This Ni-catalyzed reductive amination methodology has been applied for the amination of more complex pharmaceuticals and steroid derivatives. Detailed DFT computations have been performed for the Ni-triphos based reductive amination reaction, and they revealed that the overall reaction has an inner-sphere mechanism with H_2 metathesis as the rate determining step.



Reference : Kathiravan Murugesan, Zhihong Wei, Vishwas G. Chandrashekhar, Haijun Jiao, Matthias Beller, Rajenahally V. Jagadeesh **General and selective synthesis of primary amines using Ni-based homogeneous catalysts**_*Chem. Sci.*, 2020,11, 4332-4339

(A) Convert nitrobenzene to chlorobenzene.

(B) What happens when butanone reacts with ammonia according to scheme given above.

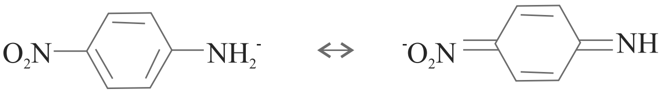
(C) Mention one method, other than mentioned here for conversion of nitrobenzene to aniline.

3. **Read the passage and answer the following questions:**

For a group of nitro-substituted anilines and diphenylamines, a plot of PICHA (ordinate) against pK_{BH^+} gave a straight line of slope 0.6. That is, the acidities of the amines seemed to be affected to a smaller extent by ring substitution than were their basicities.

$$ArNH_3^+ \xleftarrow{H^+} ArNH_2 \xrightarrow{-H^+} ArNH^-$$

This result was somewhat surprising because, although resonance with the nitro group occurs in both the neutral amine and the anion, and hence affects both equilibria, it involves a very important charge dclocalization in the amide anion.



It has been suggested that the nitro substituent has an anomalous effect in acid mixtures (2), where some of the pK_{BH^+} values had been determined. In the course of extending the H— scale to very basic values, we had the opportunity to use amines containing substituents other than nitro (3) and to determine if the unusual effect of substituents on acidity vis-a-vis basicity was due to the presence of nitro groups. In accompanying papers the pK_{BH^+} values (4) and the pK_{HA} values of these aromatic amines are reported. (The basicities of amines are described, as is customary, in terms of the acidity of their conjugate acids.)

Reference : Ross Stewart and Douglas Dolman. **A comparison of the acidity and basicity of aromatic amines**. *Canadian Journal of Chemistry.* 45(9): 925-928. https://doi.org/10.1139/v67-156

(A) Which of the following has highest pK_b value?

(a) Aniline

(b) *p*-Nitoaniline

(c) *m*-Nitroaniline

(d) *o*-Nitroaniline

(B) Why basic strength of aliphatic amines are higher than ammonia?

(C) What will be the correct order of basic strength of following: Et NH_2, $(Et)_2$ NH, $(Et)_3N$

(D) What happens when aniline reacts with sulphuric acid?

ANSWERS

I MULTIPLE CHOICE QUESTIONS

1. b 2. d 3. a 4. d 5. c 6. a 7. b 8. c 9. c 10. a
11. c 12. d 13. a 14. a 15. c 16. b. 17. a. 18. c 19. a 20. c

II FILL IN THE BLANKS

1. Aniline
2. weaker, stronger
3. Primary aliphatic
4. Hinsberg
5. Butanamine
6. Acetylation
7. *meta*
8. Water.
9. H-bonding

III ASSERTION REASON TYPE QUESTIONS

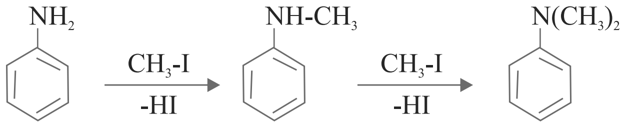
1. c 2. c 3. a 4. b 5. a 6. c 7. a 8. a 9. b 10. a

IV ONE WORD ANSWER TYPE QUESTIONS

1. Carbylamine reaction
2. 2,4,6-tribromoaniline
3. Aniline
4. weaker
5. Friedel-Crafts reaction
6. Benzene
7. Sandmeyer
8. S_N2
9. pH-9 to 10
10. Sn + HCl
11. 8
12. $LiAlH_4$
13. S_N1/S_N2
14. Pyridine

CASE STUDY BASED QUESTIONS

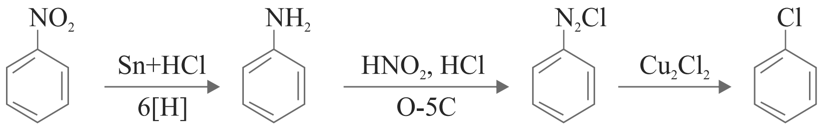
1: (A) Aniline forms salt with anhydrous $AlCl_3$.

(B) 

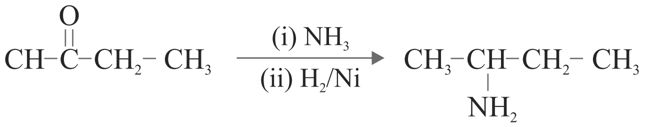
(C) Refer NCERT

(D) Due to +R effect of $-NH_2$ group.

2: (A)

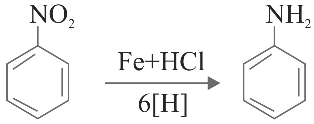


(B)



$$\mathrm{CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}\ CH_3 \xrightarrow[\text{(ii) } H_2/Ni]{\text{(i) } NH_3} CH_3{-}\underset{\underset{\displaystyle NH_2}{|}}{CH}{-}CH_2{-}\ CH_3}$$

(C)



3: (A) (d)

(B) Due to +I effect of -R groups present in aliphatic amines

(C) $(Et)_2$ NH, $(Et)_3N$, $EtNH_2$

UNIT TEST-1

Amines

Maximum Marks : 20 **Time Allowed : 1 Hour**

1. Benzamide reacts with Br_2 and NaOH forming................................. 1

2. The correct order of basicity of amines is: 1

   (a) Ammonia > Ethanamine > Aniline

   (b) Ethanaminc > Ammonia > Aniline

   (c) Ammonia > Aniline > Ethanamine

   (d) Ethanamine > Aniline > Ammonia

3. When aniline reacts with $NaNO_2$/HCl then reaction with CuCN followed by acidic hydrolysis. What will be the final product of the reaction? 1

   (a) Nitrobenzene (b) Benzaldehyde

   (c) Benzoic acid (d) Phenol

4. Assertion: Aniline forms 2,4,6-tribromoaniline on reaction with bromine water.

   Reason: -NH_2 is *ortho*, *para*- directing. 1

   (a) Both assertion and reason are correct statements and reason is correct explanation of assertion.

   (b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

   (c) Assertion is correct statement but reason is wrong statement.

   (d) Assertion is wrong statement but reason is correct statement.

5. Assertion: Primary amines cannot be synthesised by Gabriel phthalimide synthesis.

   Reason: Due to steric hindrance caused by bulky group substitution is not possible.

(a) Both assertion and reason are correct statements and reason is correct explanation of assertion. 1

   (b) Both assertion and reason are correct statements but reason is not correct explanation of assertion.

   (c) Assertion is correct statement but reason is wrong statement.

   (d) Assertion is wrong statement but reason is correct statement.

6. How will you synthesise Butanamine by Gabriel phthalimide synthesis? 2

7. Write chemical test distinguish to between following pair of compounds: 2

   (a) Aniline and Benzylamine

(b) Methylamine and Dimethylamine

8. How will you convert the following compound: 2

(a) Ethanoic acid to Methanamine

(b) Aniline to *p*-Bromoaniline

9. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula $C_6H_{13}N$. Write the structures and IUPAC names of compounds A, B and C. 3

10. Write short notes on following: 3

(a) Benzoylation reaction

(b) Hoffmann bromamide degradation reaction

(c) Carbylamine reaction

I1. Explain with suitable reason: 3

(a) Acetylation of aniline reduces its activation effect.

(b) CH_3NH_2 is more basic than CH_3CONH_2.

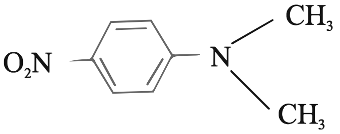
(c) Nitration of aniline gives significant amount of *meta*-Nitroaniline in addition to *o*- and *p*-Nitroaniline.

UNIT TEST-II

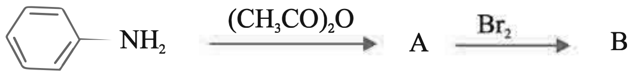
Amines

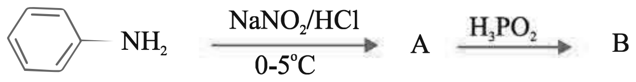
Maximum Marks : 20 **Time Allowed : 1 Hr**

1. Give the IUPAC of following compound. 1



2. Give reason:- aniline does not undergo friedel craft alkylation. 1
3. How will you convert Benzene into aniline 1
4. What is Hinsberg reagent? 1
5. Out of butan-1-ol and but-1-amine which one has higher boiling point? 1
6. Write short note on following: 2
   (i) Gabriel phthalimide synthesis
   (ii) Diazotisation
7. Write chemical distinguish test between following pair. 2
   (a) Aniline and benzylamine
   (b) Ethane amine and N, N-dimethylethanamine.
8. Complete the following reaction. 2

(i)


(ii)


9. Arrange the following as per mentioned properties. 3
   (a) Ethaneamine, N-ethylthaneamine, N-N-diethylethnanamine (Basic strength in aqueous medium)
   (b) Aniline, *p*-Nitroaniline, *p*-Toluidine(increasing basic character)
   (c) $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$ – increasing order of solubility in water.
10. Convert the following compounds: 3
    (a) Benzamide to Toluene
    (b) Aniline to 2,4,6 - Tribromofluorobenzene
    (c) Chlorobenzene to *p*-chloroaniline.
11. Two isomeric compound 'A' and 'B' having molecular formula $C_4H_{11}N$, both lose N_2 on treatment with HNO_2 and gives compound 'C' and 'D' respectively. 'C' is resistant to oxidation but immediately respond to Lucas reagent. Whereas 'D' respond to Lucas reagent after 5 minutes and gives a positive iodoform test. Identify A, B, C, D. 3