

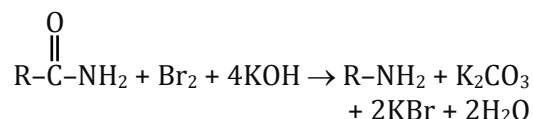
Amines

SOLUTIONS

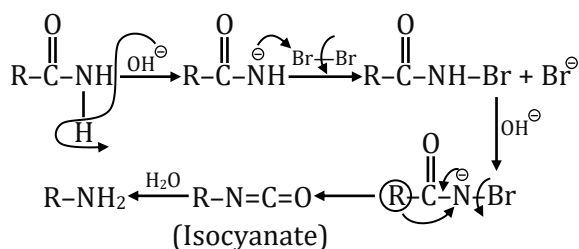
Exercise-I (Conceptual Questions)

1. **Ans. (4)**

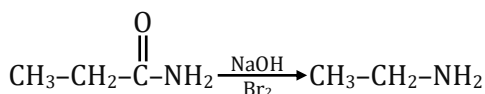
Hoffmann bromamide degradation reaction



Mechanism:-



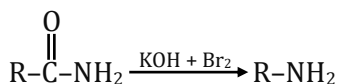
Therefore, R-NC is not formed in the Hoffmann Bromamide degradation reaction.

2. **Ans. (2)**

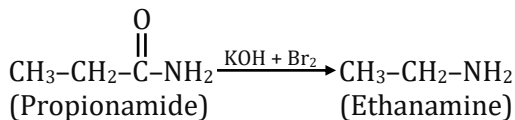
Since product obtained is amine which is basic in nature, it turns red litmus to blue.

3. **Ans. (3)**

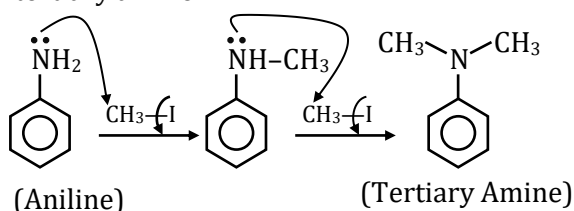
In Hoffmann bromamide degradation reaction.



The total number of carbons in product is reduced by one carbon.

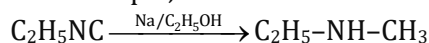
 $\therefore$ To obtain Ethanamine as product,4. **Ans. (1)**

Tertiary amine :- when nitrogen is directly attached with three carbons, it is called tertiary amine

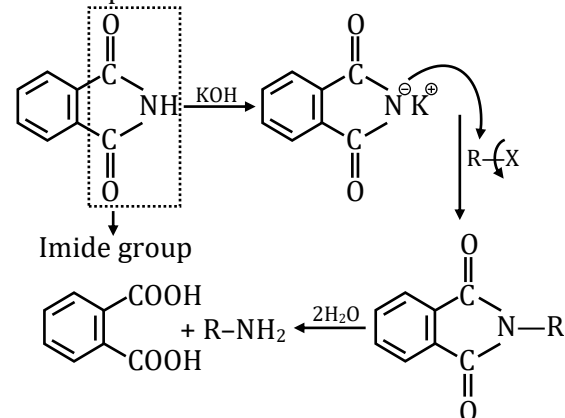
5. **Ans. (3)**

Reduction of Alkyl Isocyanides gives secondary amines

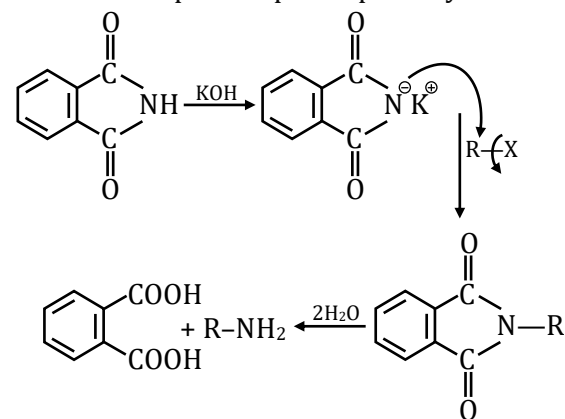
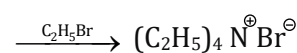
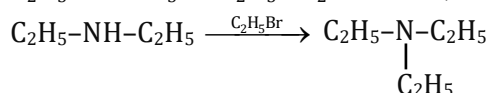
For Example,

6. **Ans. (3)**

Gabriel phthalimide reaction

7. **Ans. (3)**

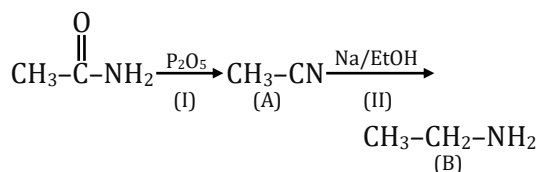
Gabriel phthalimide reaction is used in the formation of pure Aliphatic primary amines.

8. **Ans. (3)**

(Quaternary ammonium salt)

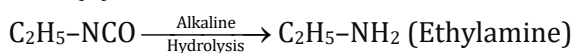
The above reaction is called ammonolysis and also it involves attack of ammonia as a Nucleophile which substitutes -Br, Therefore, it is also an example of nucleophilic substitution.

9. **Ans. (3)**

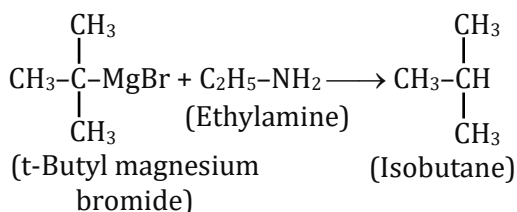


Therefore, the given reaction II is Mendius reaction which involves the reduction of the organic compound containing the cyanide group in the presence of an alkali metal and alcohol which results in the formation of amines.

10. **Ans. (3)**

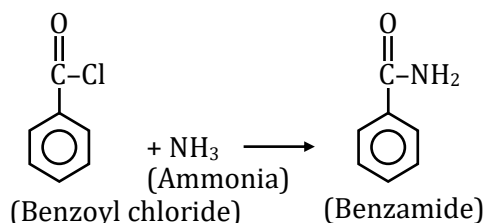


When ethylamine is treated with t-butyl magnesium bromide, the compound obtained will be Isobutane.

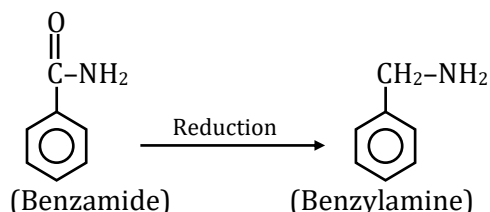


11. **Ans. (3)**

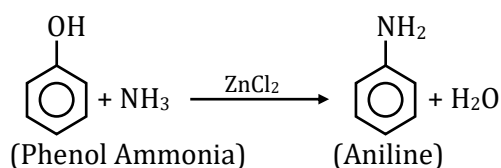
Option 1 : Benzoyl chloride and ammonia



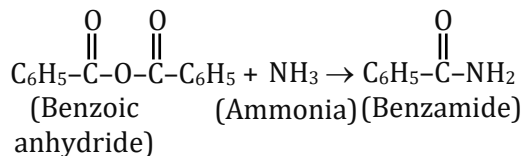
Option 2 : Reduction of benzamide



Option 3 : Phenol and ammonia in presence of ZnCl_2



Option 4 : Benzoic Anhydride and ammonia



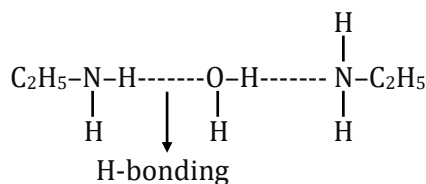
12. **Ans. (3)**

Primary amide	Secondary amide	Tertiary amide
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{H} \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{R}' \\ \\ \text{H} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{N}-\text{R}' \\ \\ \text{R}'' \end{array}$
Two H can participate in H-bonding with another molecule	Only one H can participate in H-bonding	No H-bonding

Therefore, primary amides have maximum boiling point

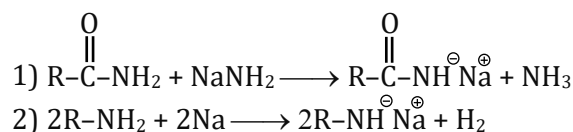
13. **Ans. (3)**

Ethylamine in water shows H-bonding which involves formation of H-bond with water.



Therefore, solubility of ethylamine is due to formation of H-bonding with water.

14. **Ans. (3)**



Therefore, the hydrogen attached to nitrogen is released in both of the above reaction.

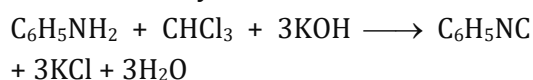
15. **Ans. (2)**

$\text{C}_2\text{H}_5-\text{NH}-\text{C}_2\text{H}_5$ is a secondary amine, therefore, it will not give carbylamine test.

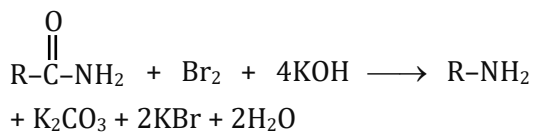
16. **Ans. (4)**

Chloroform and ethanolic KOH can be used as a reagent in the following reactions.

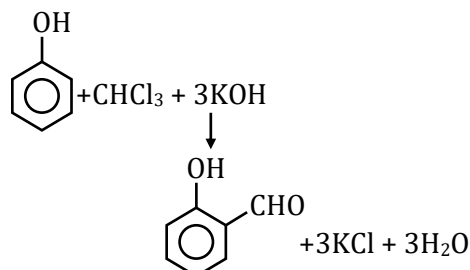
(a) Hoffmann carbylamine reaction



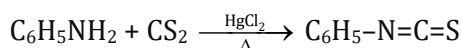
(b) Hoffmann degradation reaction



(c) Reimer-Tiemann reaction

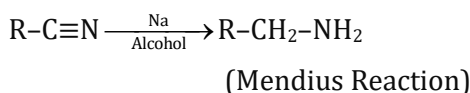


(d) Hoffmann mustard oil reaction



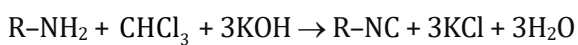
Therefore, option 4 only a & c is correct.

17. **Ans. (3)**



18. **Ans. (1)**

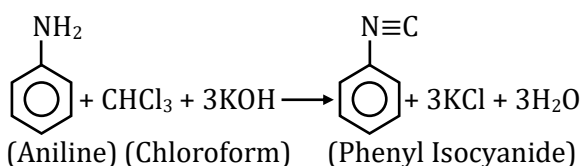
Carbylamine Test



(Primary amine)

(Alkyl Isocyanide)

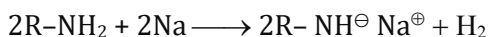
19. **Ans. (1)**



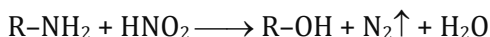
20. **Ans. (2)**

Acidic nature of amines is shown by its acidic hydrogen.

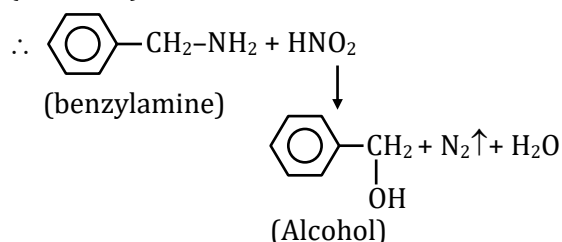
For example :-



21. **Ans. (2)**

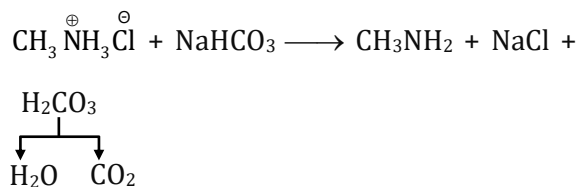


(1° amine)



22. **Ans. (4)**

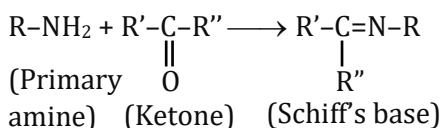
$\text{CH}_3\text{NH}_3^\oplus\text{Cl}^\ominus$ will react with NaHCO_3 to give H_2CO_3 which further liberates CO_2 and H_2O



Note:- Amines and Alcohols are less acidic than H_2CO_3 , therefore they will not react with NaHCO_3 .

23. **Ans. (4)**

When primary amines are treated with ketone, schiff's base is obtained.



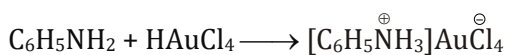
24. **Ans. (4)**

Since $\text{RNH}_3^\oplus\text{Cl}^\ominus$ is an acidic salt, it turns blue litmus into red.

Note:- $\text{R}-\text{OH}$, $\text{R}-\text{NH}_2$ & $\text{R}-\text{NH}_3^\oplus\text{OH}^\ominus$ are basic in nature.

25. **Ans. (3)**

In the given reaction



Here, $-\text{NH}_2$ group of Aniline donates e^-

Pair to HAuCl_4 , Therefore It acts as Lewis base. So, Aniline shows basic nature.

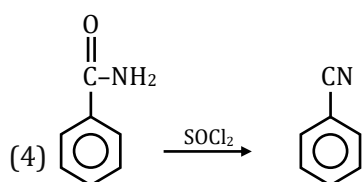
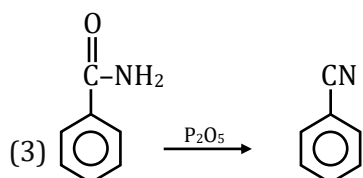
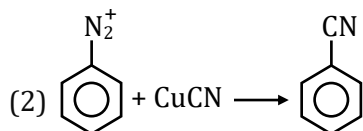
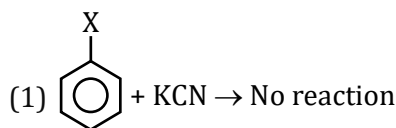
26. **Ans. (4)**

Tollen's reagent $\rightarrow$ Ammonical silver nitrate solution

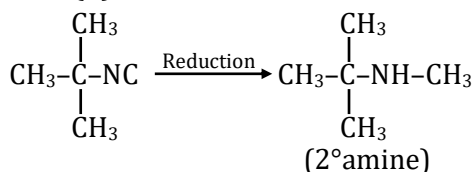
Aldehydes, Alpha Hydroxy Ketones and Formic acid are able to give Tollen's test.

$\text{C}_6\text{H}_5\text{NH}_2$ will not reduce Tollen's reagent.

27. Ans. (1)



28. Ans. (2)



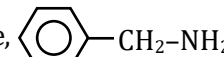
29. Ans. (2)

Nitrobenzene can't show F.C.R. so nitrobenzene can act as solvent in Friedel craft reaction.

Aniline form salt in product.

Toluene and Benzene show FCR so that can't be used as solvent in FCR.

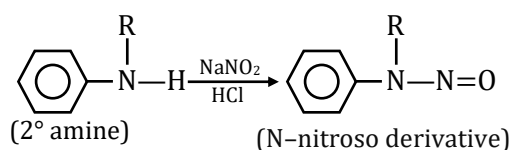
30. Ans. (4)

For Diazo coupling reaction, we require diazonium salt to be coupled with highly activated aromatic compound like aniline phenol, β -Naphthol therefore, 

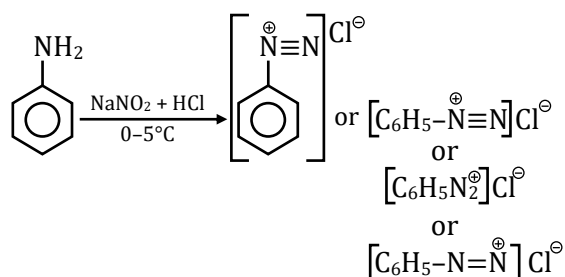
does not show diazo coupling reaction due to +H effect of $-\text{CH}_2\text{NH}_2$ group as it activate the ring less as compared to other given groups.

31. Ans. (3)

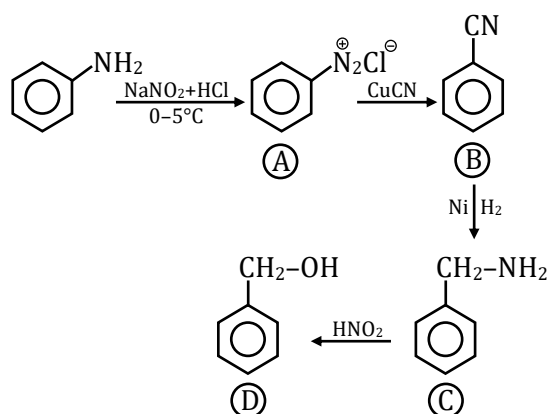
Secondary amines form N-nitroso derivative when treated with NaNO_2 and HCl



32. Ans. (4)

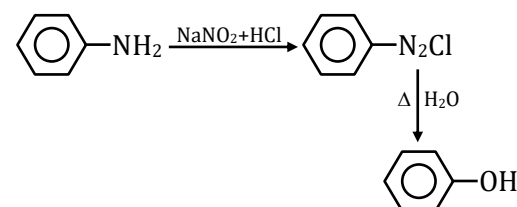


33. Ans. (1)



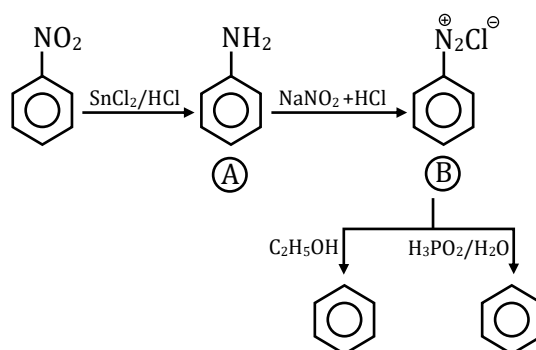
$\therefore$ Structure of product D is $\text{C}_6\text{H}_5-\text{CH}_2-\text{OH}$

34. Ans. (2)



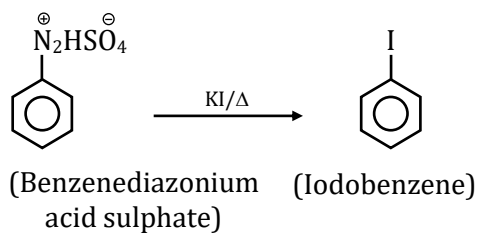
$\therefore$ X is $-\text{NH}_2$
Y is $-\text{OH}$ } $\rightarrow$ Both are O & P directing.

35. Ans. (3)



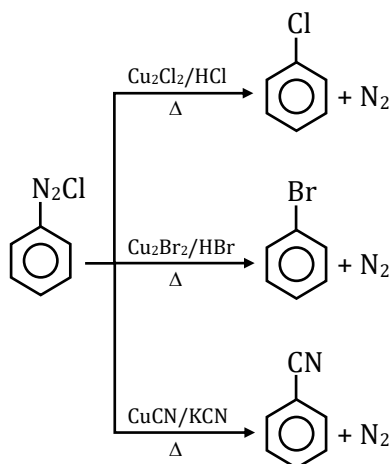
$\therefore$ From B, Benzene can be obtained by using ethanol as well as H_3PO_2 .

36. Ans. (3)

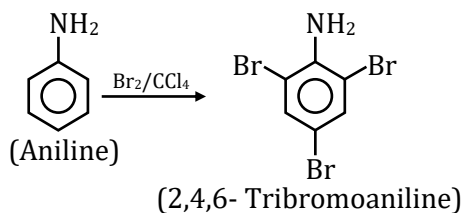


37. Ans. (1)

In Sandmeyer's reaction, $-N=N-X$ group of diazonium salt is replaced by Halide group.

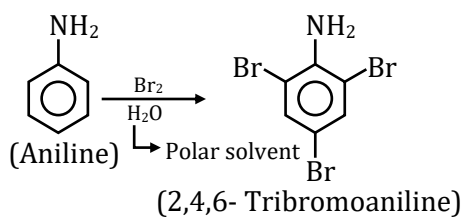


38. Ans. (2)



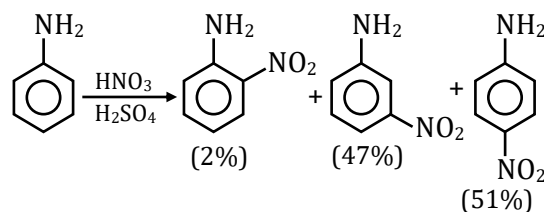
Note:- Since, $-NH_2$ is a highly Activating group it is O & P directing and we get trisubstituted aniline.

39. Ans. (3)



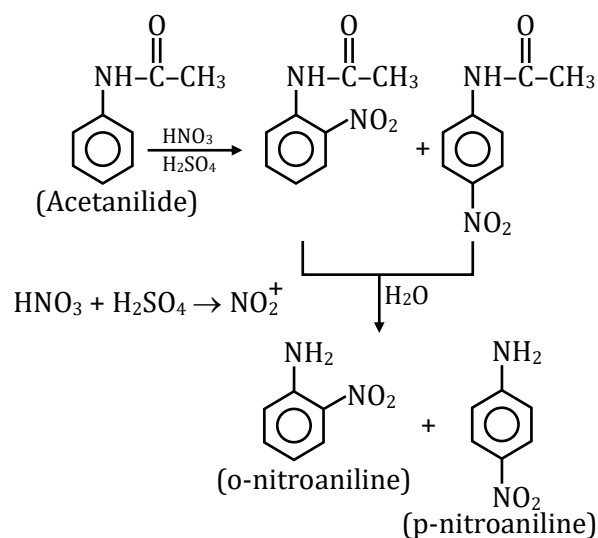
Note:- Since, $-NH_2$ is a highly Activating group it is O & P directing and we get trisubstituted aniline.

40. Ans. (4)

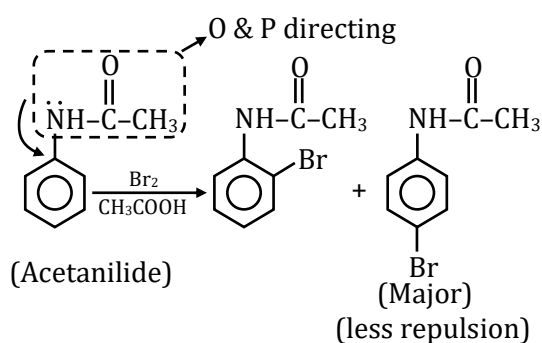


Meta substitution is also take place due to the formation of anilium ion.

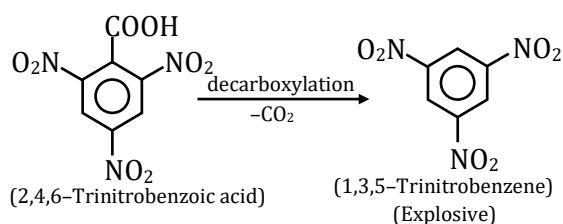
41. Ans. (3)



42. Ans. (3)

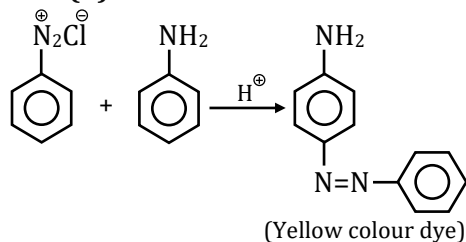


43. Ans. (1)



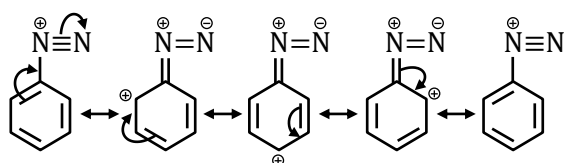
Exercise-II (Previous Year Questions)

1. Ans. (4)

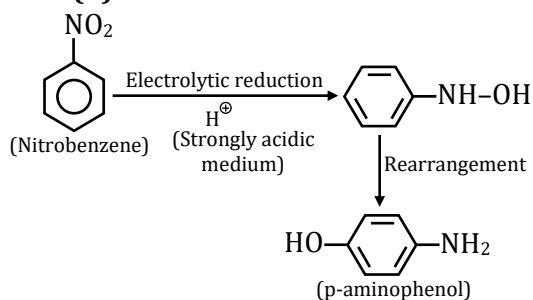


2. Ans. (2)

Among all the given four options, $C_6H_5 N_2^+ X^-$ is the most stable diazonium salt because it shows resonance.

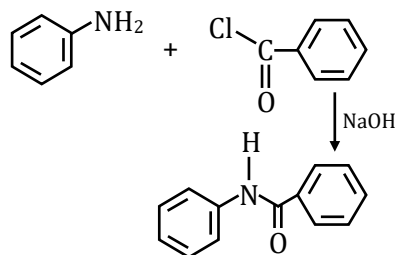


3. Ans. (4)



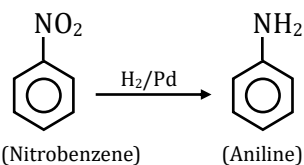
4. Ans. (2)

→ Benzoylation of amine is an example of Schotten-Baumann reaction.

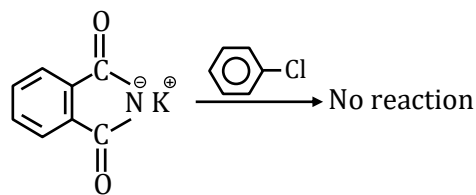


5. Ans. (2)

(1) Reduction of Nitrobenzene with H_2/Pd in ethanol

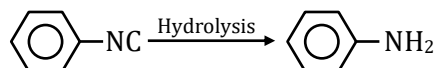


(2) Potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous NaOH solution.

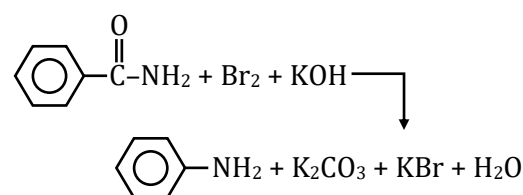


In Gabriel phthalimide reaction, Aniline cannot be formed.

(3) Hydrolysis of phenyl isocyanide with acidic solution.

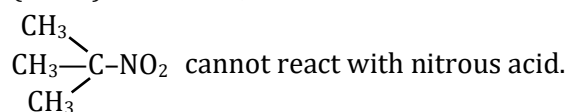


(4) Degradation of benzamide with bromine in alkaline solution.

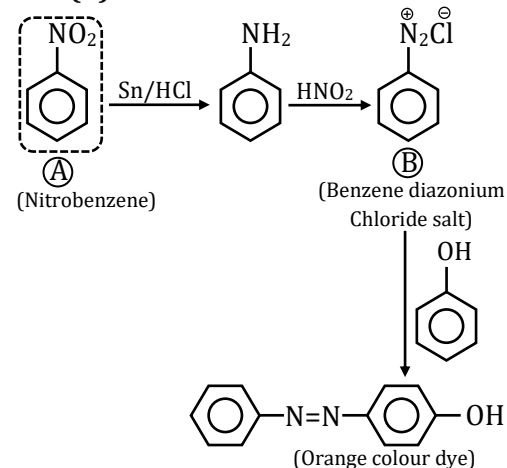


6. Ans. (1)

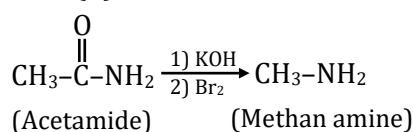
The nitro compounds which contains atleast one active H (α -H) can react with nitrous acid (HNO_2). Therefore,



7. Ans. (4)

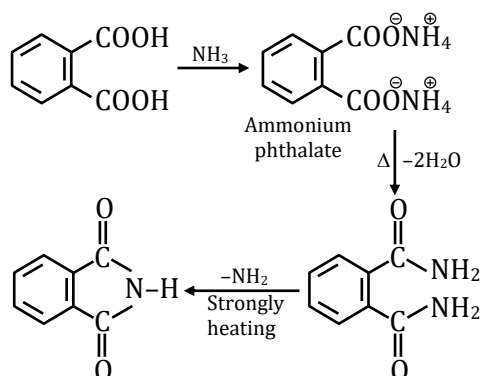


8. Ans. (1)



∴ Hoffmann hypobromamide reaction is appropriate for above conversion.

9. Ans. (2)



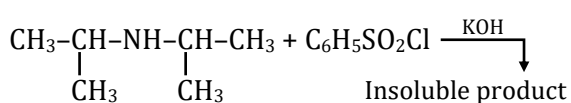
10. Ans. (1)

In Hinsberg method, mixture of amines is separated by using benzene sulphonyl chloride (Hinsberg reagent)

$\text{C}_6\text{H}_5\text{SO}_2\text{Cl} + 1^\circ \text{ amine} \rightarrow \text{Product} \xrightarrow{\text{KOH}}$ soluble (PPT.)

$\text{C}_6\text{H}_5\text{SO}_2\text{Cl} + 2^\circ \text{ amine} \rightarrow \text{Product} \xrightarrow{\text{KOH}}$ insoluble. (PPT.)

$\therefore$ Option 1 represents secondary amine

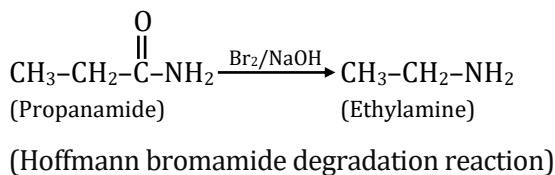


11. Ans. (2)

Carbylamine test is generally used to detect primary amines and it is also given by aniline.



12. Ans. (1)

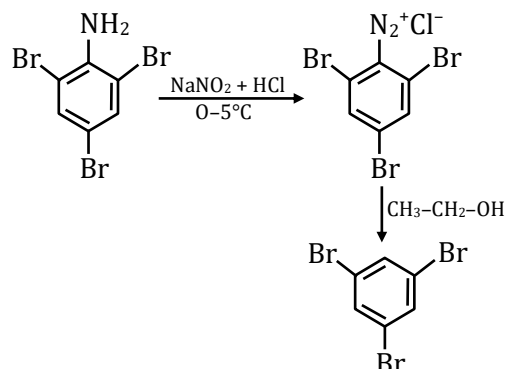


13. Ans. (3)

When primary amine is treated with Hinsberg reagent, it gives soluble product with base.

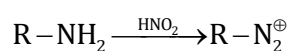
$\therefore \text{CH}_3-\text{CH}_2-\text{NH}_2$ will react with Hinsberg's reagent to give a solid which dissolves in alkali.

14. Ans. (2)

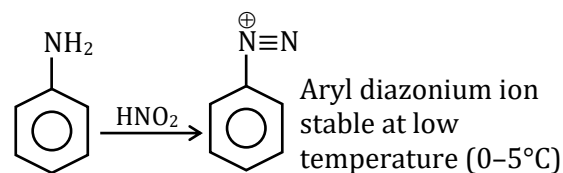


$\therefore \text{R} \rightarrow \text{CH}_3-\text{CH}_2-\text{OH}$

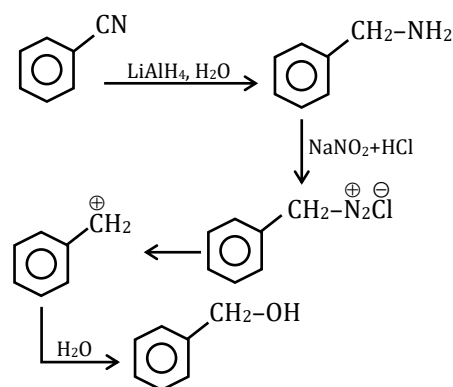
15. Ans. (2)



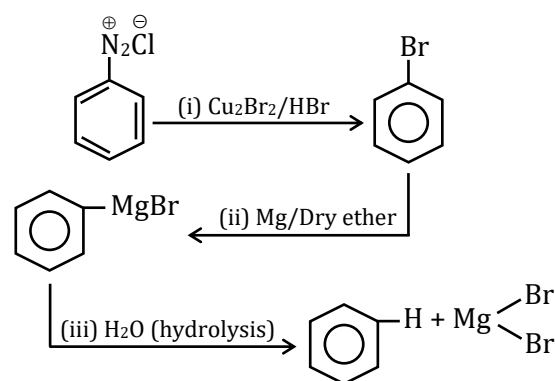
Alkyl diazonium ion (unstable)



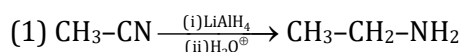
16. Ans. (3)



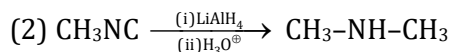
17. Ans. (1)



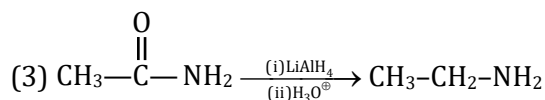
18. Ans. (2)



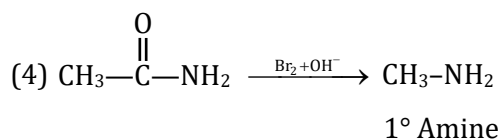
1° Amine



2° Amine

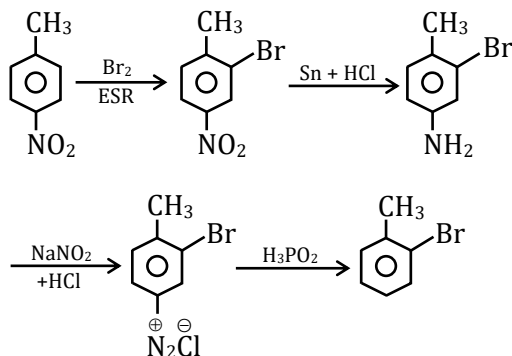


1° Amine



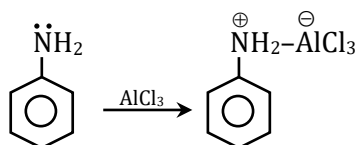
1° Amine

19. Ans. (3)



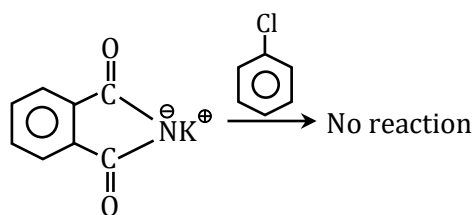
20. Ans. (1)

Statement-I :- Explanation : Aniline forms complex with Lewis acid (AlCl_3),

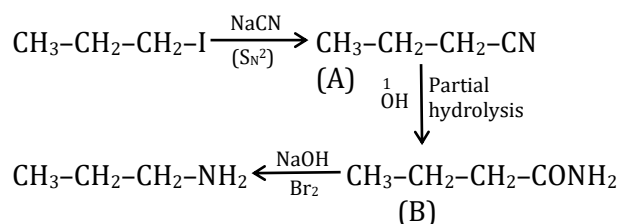


So statement-I is correct.

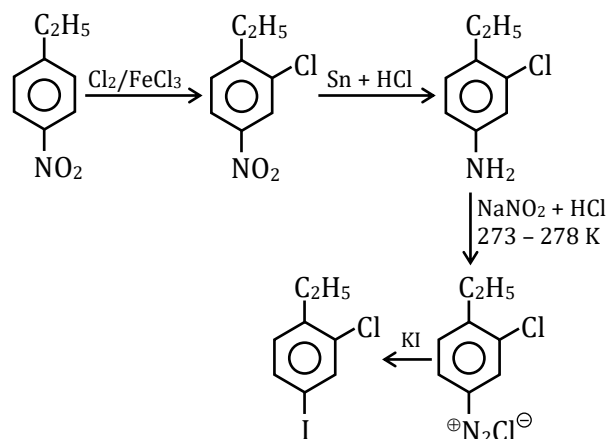
Statement-II :- Explanation : Aryl halide are not good substrate for nucleophilic substitution reaction so aniline does not give Gabriel synthesis.



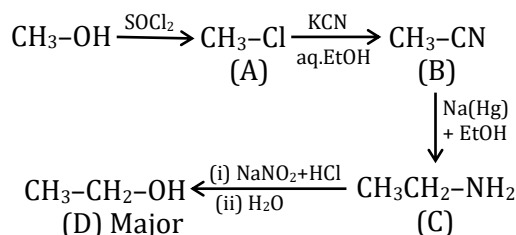
21. Ans. (1)



22. Ans. (3)

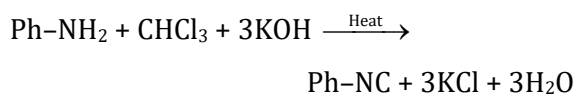


23. Ans. (3)



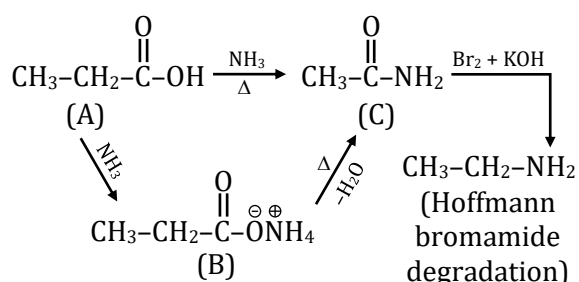
24. Ans. (1)

Aniline does not show FCR but gives positive carbyl amine test.



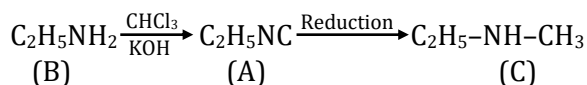
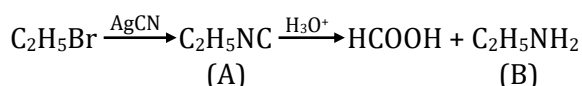
Exercise-III (Analytical Questions)

1. Ans. (4)



Amines

2. Ans. (4)

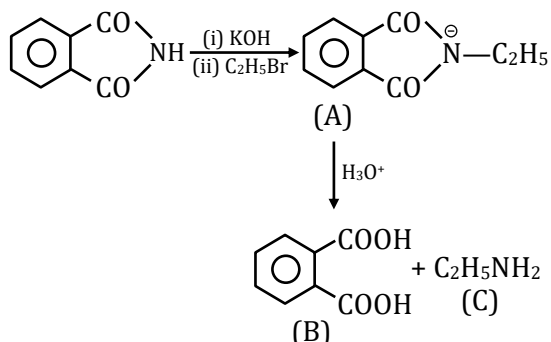


(A) → Carbylamino Ethane

(B) → Ethanamine

(C) → Ethyl methyl amine

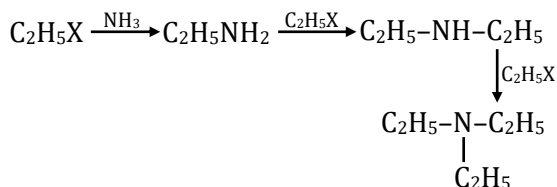
3. Ans. (2)



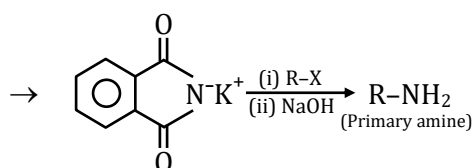
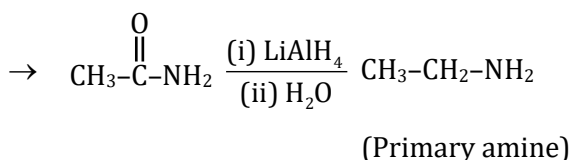
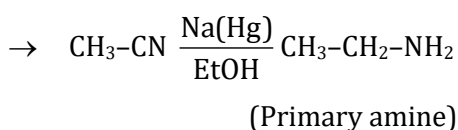
(B) → phthalic acid

(C) → Ethyl amine

4. Ans. (1)



∴ In option 1, mixture of amine will be obtained.



∴ Option 1 is correct

5. Ans. (3)

→ Carbylamine reaction can be used to identify primary amino group in any given compound

→ Victor Meyer's is used to detect type of Alcohols.

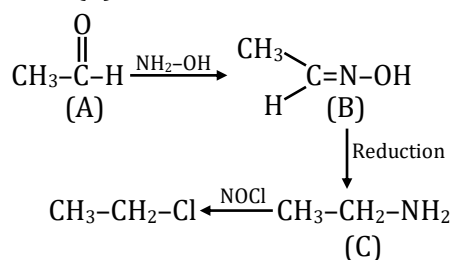
→ Iodoform test are the test given by aldehyde & ketones in which methyl keto $\left(\text{CH}_3\text{-C(=O)-}\right)$ is present.

6. Ans. (1)

In amines, as the number of alkyl group on ammonium cation, the stability of ammonium action decreases because alkyl group provides steric hinderance to the water molecule from forming H-bonding in water for alkyl substituted ammonium cation will be



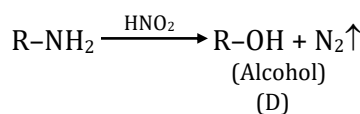
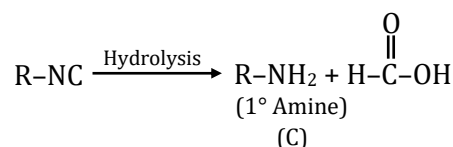
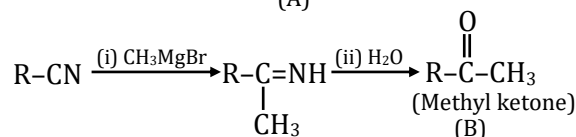
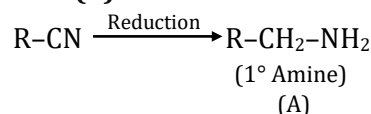
7. Ans. (4)



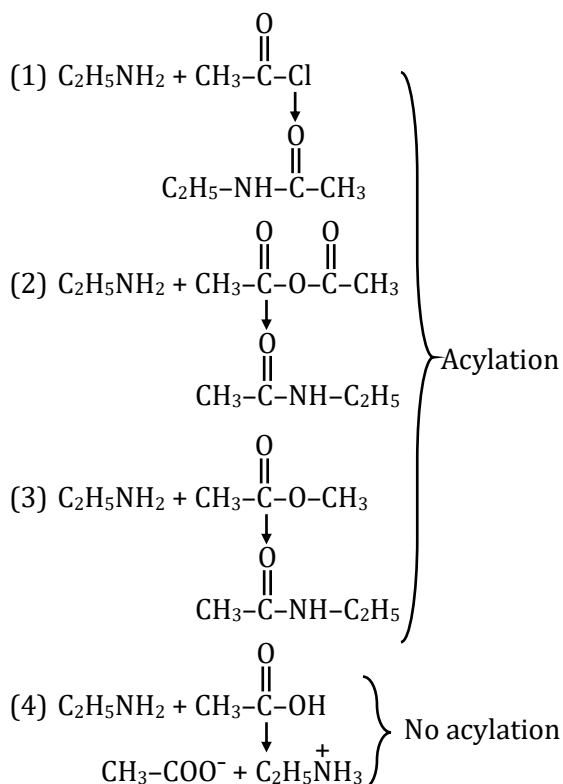
8. Ans. (4)

Basic nature of amine in aqueous medium can be explained by Inductive effect, solvation effect and steric hinderance.

9. Ans. (2)

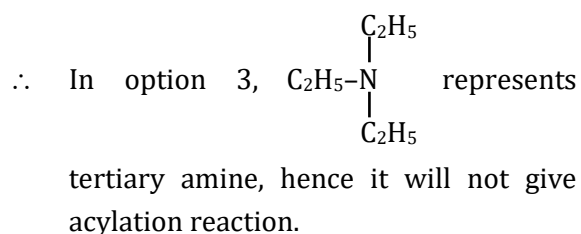


10. Ans. (4)

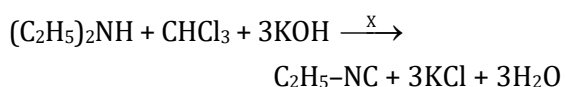


11. Ans. (3)

Tertiary amines are unable to give acylation reaction due to steric hinderance.



12. Ans. (3)

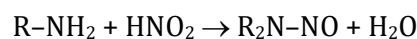
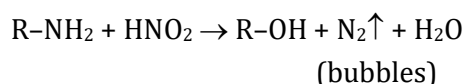


It is incorrect reaction because $(\text{C}_2\text{H}_5)_2\text{NH}$ represents a secondary amine and carbylamine reaction is used to detect primary amines.

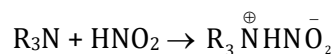
13. Ans. (4)

To distinguish primary, secondary and tertiary amine, following reaction can be used.

(a) Reaction with Nitrous acid



Dialkyl nitrosoamine (bubbles)

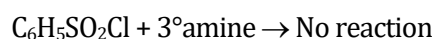
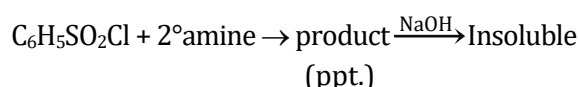
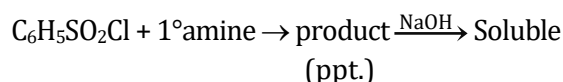


Trialkyl ammonium Nitrate

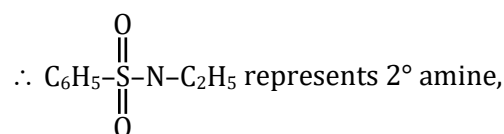
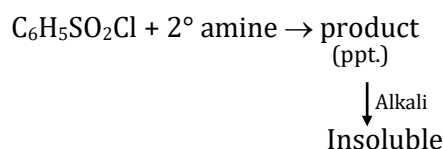
(Soluble in water)

(b) Reaction with Hinsberg reagent

Following by NaOH

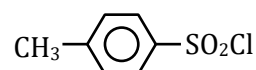


14. Ans. (1)

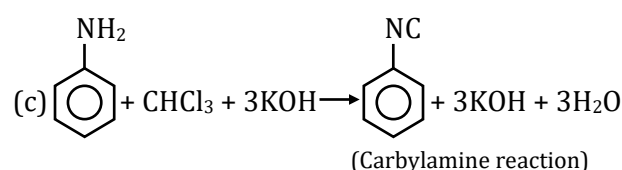
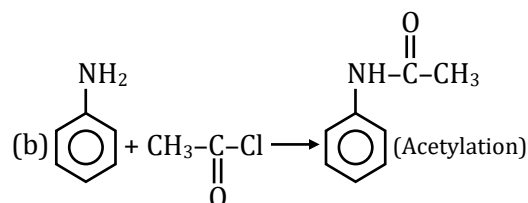
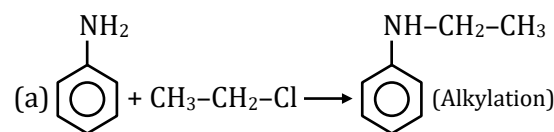


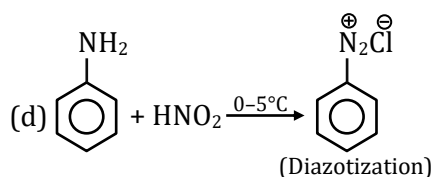
15. Ans. (3)

In Hinsberg test, Benzene sulphonyl chloride is replaced by p-toluene sulphonyl chloride.



16. Ans. (1)





(p) → Acetylation (q) → Alkylation

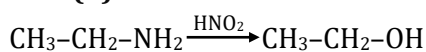
(r) → Diazotization (s) → Carbylamine reaction

(t) → Halogenation

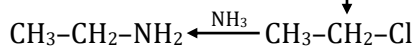
∴ Correct answer is

$$(a) \rightarrow (q), (b) \rightarrow (p), (c) \rightarrow (s), (d) \rightarrow (r)$$

17. Ans. (2)



(A)

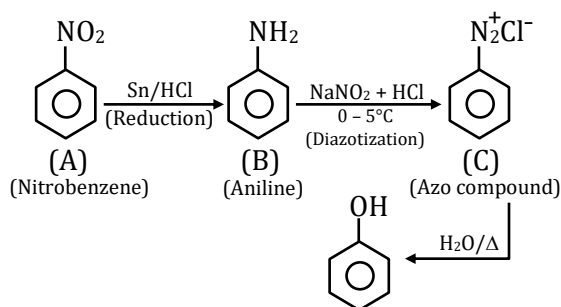


(C)

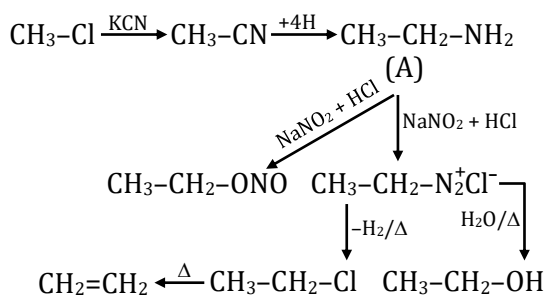
(B)

∴ End product (C) will be Ethylamine.

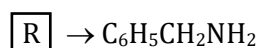
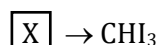
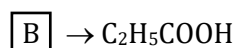
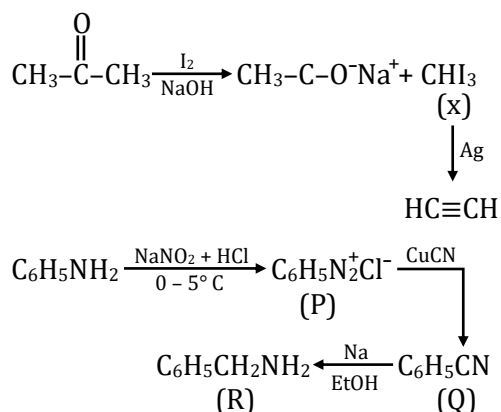
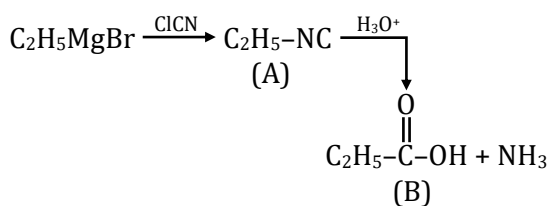
18. Ans. (2)



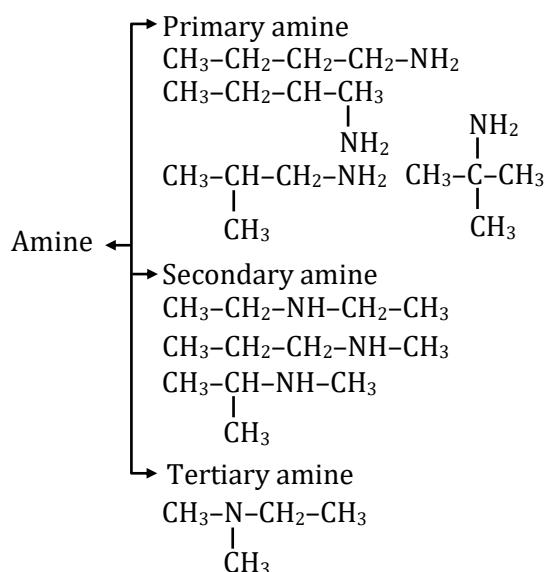
19. Ans. (4)



20. Ans. (1)



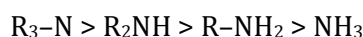
21. Ans. (2)

Molecular Formula = C₄H₁₁N
$$\text{D.U.} = 0$$


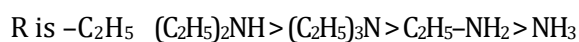
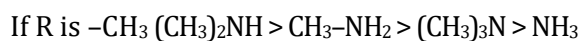
∴ Total structural isomeric amines for $C_4H_{11}N = 8$

22. Ans. (3)

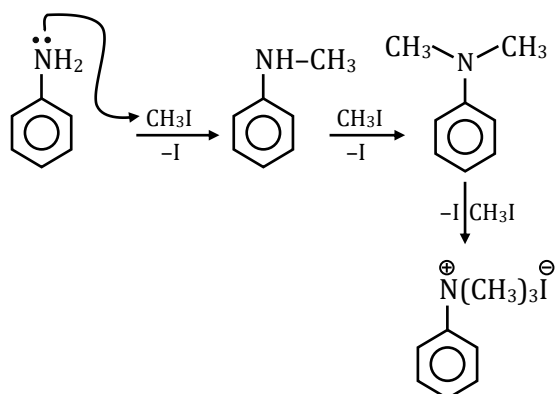
Basic strength of amines in gaseous solution



Basic strength of amines in an aq. solution



23. Ans. (4)

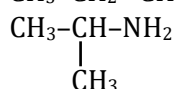
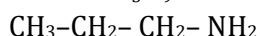


24. Ans. (1)

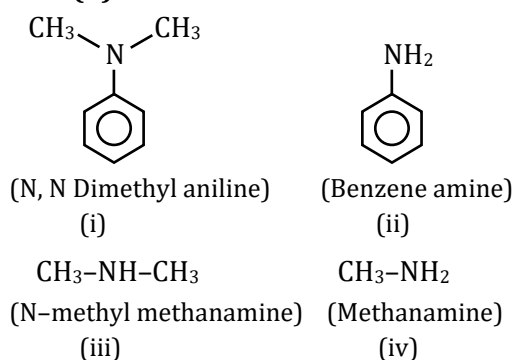
Molecular Formula :- C_3H_9N

→ Primary amines when treated with HNO_2 gives alcohol and liberate N_2 gas.

→ Different primary amines with molecular formula C_3H_9N are 2.



25. Ans. (3)



∴ Order of basic strength :-

(iii) > (iv) > (i) > (ii)

∴ Given values of pK_b :-

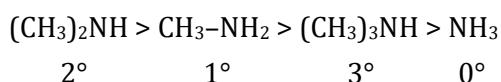
$a = 9.38, b = 8.92, c = 3.38, d = 3.27$

$$\text{Basic strength} \propto \frac{1}{pK_b}$$

∴ (i) → b, (ii) → a, (iii) → d, (iv) → c

26. Ans. (3)

Order of basic medium in aqueous medium can be defined by more than one type of effects.



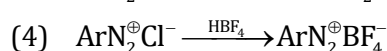
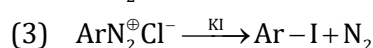
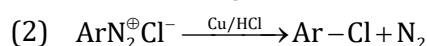
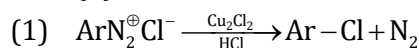
More substituted ammonium ion gets stabilised due to I effect of alkyl group as it increases the availability of electrons to donate but on the other hand, more the number of Alkyl groups, more will be the steric hinderance to H-bonding in ammonium ion which decreases the solvation effect.

∴ a, c, d are correct.

27. Ans. (2)

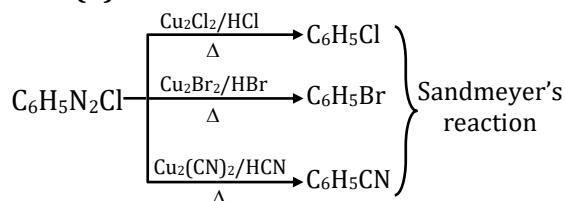
Benzene diazonium fluoroborate ($C_6H_5N_2^+ BF_4^-$) is water insoluble because it is non-polar and it is also stable as diazonium ion is resonance stabilised.

28. Ans. (4)



∴ reaction 4 do not displace N_2 from benzenediazonium salt.

29. Ans. (4)



Therefore, -I group can never be introduced in sandmeyer's reaction.

30. Ans. (4)

As we know, in diazocoupling reaction, Benzene diazonium salt reacts highly activated aromatic rings to form colour dyes.

∴ Aniline can give diazo coupling reaction but benzylamine cannot due to +M effect of $-NH_2$ group.

∴ Ethylamine can not give diazocoupling reaction but N-methyl aniline can give due to +M effect of $-NH_2$ group.

∴ Aniline and phenol both can give azo dye test but can be distinguish by the colour of dye.

Aniline when treated with benzene diazonium salt gives yellow dye whereas phenol gives orange dye.

