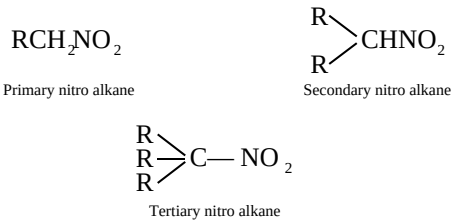
Organic Compounds Containing Nitrogen

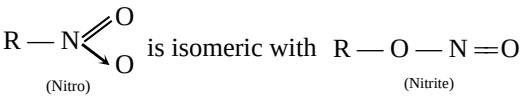
Nitro alkanes are derivatives of alkanes. They are isomeric to nitrites (esters) classified as primary, secondary and tertiary depending on the nature of carbon atom to which nitro group is linked.



Primary nitro alkane | Secondary nitro alkane | Tertiary nitro alkane

$-NO_2$ group is an ambident group.

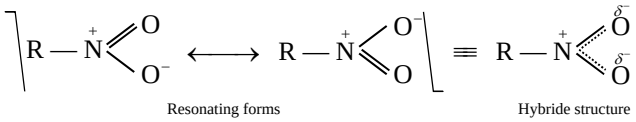
If it attacks through $\left(-N\begin{matrix}O\\O\end{matrix}\right)$ nitrogen it is called nitro and if it attacks through oxygen atom, it is called nitrite. Hence nitrites and nitro compounds are isomers.



(Nitro) is isomeric with (Nitrite)

Structures

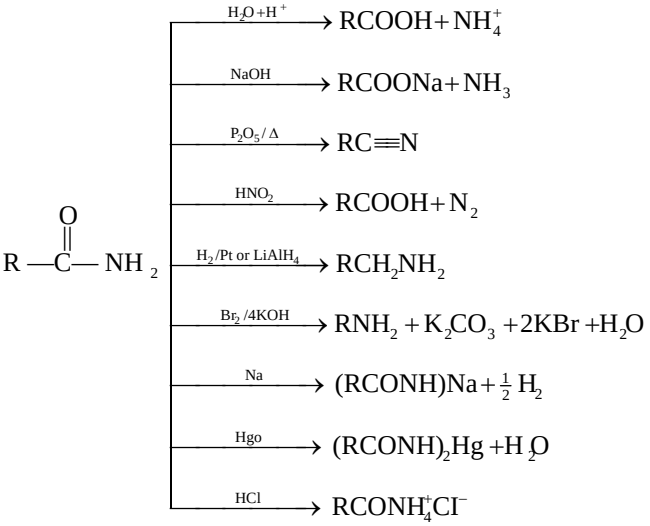
Evidences show that nitrogen is attached to one of the oxygen atoms by a double bond and to the other by a dative bond. The resonance hybrid is shown as under which confirms the spectroscopic evidence that both nitrogen –oxygen bonds have same bond length.



Resonating forms | Hybride structure

Out of three sp^2 hybrid orbitals of nitrogen one overlaps with alkyl group and two with oxygens while the unhybridised p-orbital of N-atom containing a pair of electrons and lying perpendicular to the plane of hybrid orbitals overlaps sideway with half filled 2p-orbitals of two oxygen atoms. This forms π-bond above and below the plane of molecule.

Amides



Cyanides (RCN) and Isocyanides (RNC): These are the compounds containing $-C\equiv N$ functional group.
They have general formula $R-C\equiv N$.

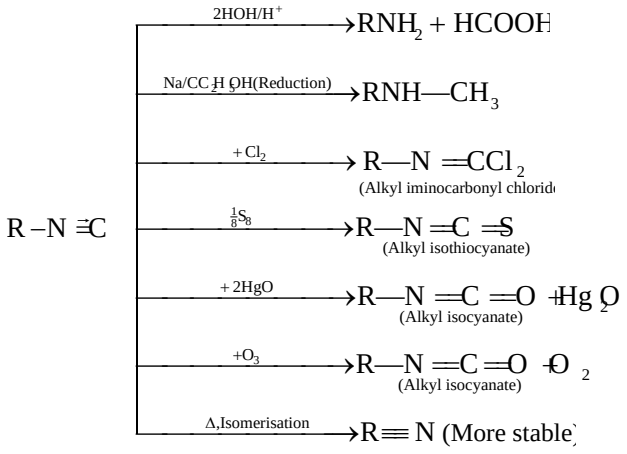
Preparation of Cyanides: The following methods can be employed to prepare the cynides.

- $RX + KCN(alc) \longrightarrow \underset{\text{(Main product)}}{RCN} + KX$
- Aryl cyanides cannot be prepared by this method because aryl halides are less reactive towards nucleophilic substitution.
- $RCONH_2 + P_2O_5 \xrightarrow{\text{Heat}} RCN + H_2O$
- $C_6H_5N_2^+Cl^- + CuCN \xrightarrow{KCN} C_6H_5CN + CuCl$
- $RCH=NOH \xrightarrow[\text{(Aldoxime)}]{(CH_3CO)_2O/\ \Delta} RC\equiv N + H_2O$
- $RMgX + ClCN \xrightarrow{\text{Dry/ether}} R-C\equiv N + Mg(Cl)X$

Preparation of Isocyanides

- $RX + AgCN \xrightarrow{C_2H_5OH} \underset{\text{(Major product)}}{RNC} + AgX$
- $RNH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} RNC + 3KCl + 3H_2O$
  (Carbylamine reaction)

Reactions of Isocyanides: Some of the important reactions of isocyanides are given below:

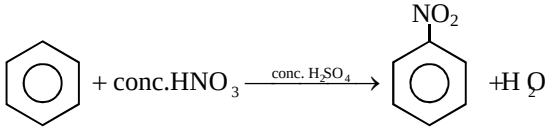


Nitro Compounds (RNO_2)

Preparation of Aliphatic nitro Compounds

- $2RX + 2AgNO_2 \xrightarrow[\text{Heat}]{\text{Alcohol}} \underset{\text{Nitroalkane (Major)}}{RNO_2} + \underset{\text{Alkyl nitrite (Minor)}}{R-O-N=O}$
- $\underset{\text{(X may be Br or I)}}{2RX} + 2K^+(O-N=O) \longrightarrow \underset{\text{Alkyl nitrite (Minor)}}{R-O-N=O} + \underset{\text{Nitroalkane (Major)}}{RNO_2}$
- $\underset{\text{Vapour}}{CH_3-CH_3} + \underset{\text{Fuming}}{HNO_3} \xrightarrow{700K} \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + H_2O$

Preparation of Aromatic Nitro Compounds: They are obtained by nitration of arenes with nitrating mixture $(H_2SO_4 + HNO_3)$.



This chemical reaction is typical example of electrophilic ring substitution. Here, conc. H_2SO_4 reacts with HNO_3 to produce nitronium ion (NO_2^+) which acts as an electrophile while ar ene behaves as the nucleophile.

Amines: These are derivatives of ammonia. They can be classified into primary, secondary or tertiary amines if they have functional groups $-NH_2$, $-\underset{|}{NH}-$, $-\underset{|}{\overset{|}{N}}-$ respectively.

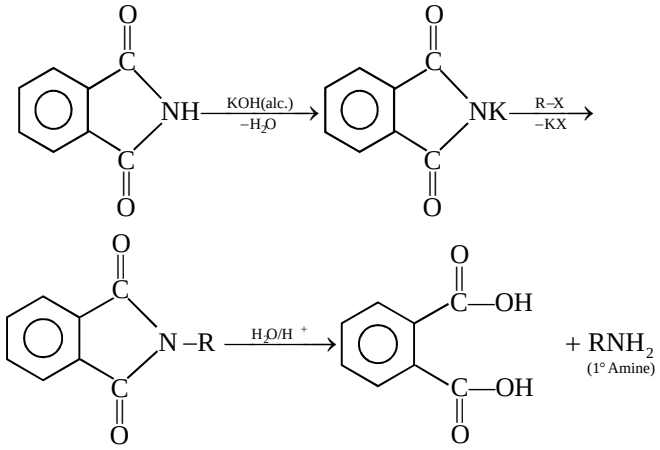
Alkyl amines: RNH_2,

Aryl amines: $ArNH_2$ (e.g. $C_6H_5NH_2$),

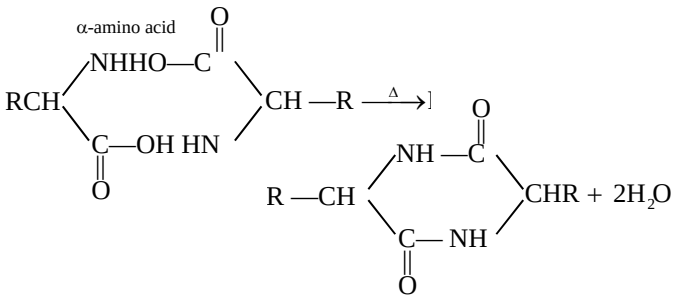
Arylalkyl amines: $ArCH_2NH_2$ (e.g., $C_6H_5CH_2NH_2$)

Preparation of Amines

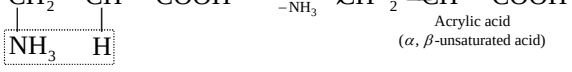
- Reduction of alkyl cyanides:
  $RCN + (H_2/Ni \text{ or } LiAlH_4) \longrightarrow RCH_2NH_2$ (1°Amine)
- Reduction of isocyanides:
  $RNC + H_2/Pt \longrightarrow RNHCH_3$ (2° Amine)
- Reduction of alkanamides:
  $RCONH_2 + (H_2/Pt \text{ or } LiAlH_4) \longrightarrow RCH_2NH_2$
- Reduction of aldoximes:
  $RCH=NOH + 4[H] \xrightarrow[\text{or } LiAlH_4]{\text{Na/alc. or } H_2/Pt} RCH_2NH_2 + H_2O$
- Hydrolysis of isocyanate:
  $R-N=C=O + 2KOH \longrightarrow RNH_2 + K_2CO_3$
- Hoffmann's bromamide reaction:
  $\underset{\text{Amide}}{RCONH_2} + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$
- Hydrolysis of isocyanides:
  $RNC + HOH \xrightarrow{HCl} RNH_2 + HCOOH$
- Ammonolysis of halides: $RX + \underset{\text{(Excess)}}{NH_3} \longrightarrow RNH_2 + HX$
- Ammonolysis of alcohols:
  $ROH + NH_3 \xrightarrow{575K,\ Al_2O_3} RNH_2 + H_2O$
- Reduction of nitro compounds:
  $C_6H_5NO_2 + 6[H] \xrightarrow{Sn/HCl} C_6H_5NH_2$
- Gabriel's Phthalimide synthesis



Action of Heat: α-amino acids lose two molecules of water and form cyclic amides.

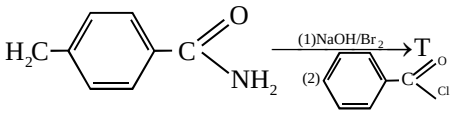


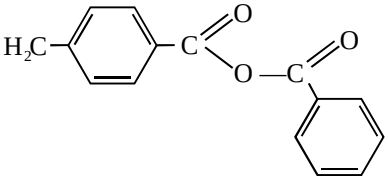
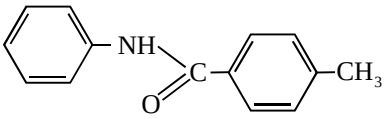
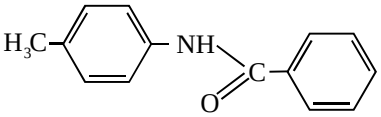
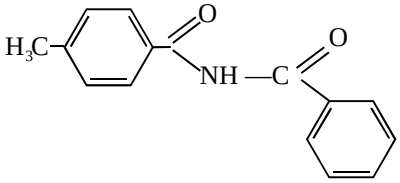
β-amino acids lose a molecule of ammonia per molecule of amino acid to yield α,β-unsaturated acids.



Multiple Choice Questions

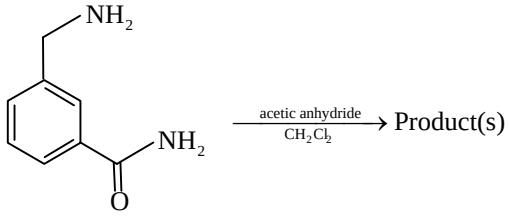
1. $CH_3NH_2 + CHCl_3 + KOH \longrightarrow$ Nitrogen containing compound $+ KCl + H_2O$. Nitrogen containing compound is
   (a) $CH_3 - C \equiv N$ (b) $CH_3 - NH - CH_3$
   (c) $CH_3 - \bar{N} \equiv \overset{+}{C}$ (d) $CH_3\overset{+}{N} \equiv \bar{C}$

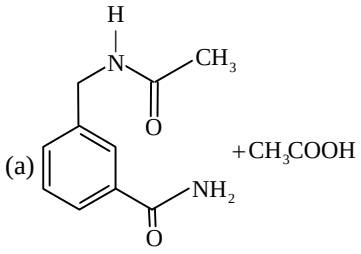
2. In the reaction 

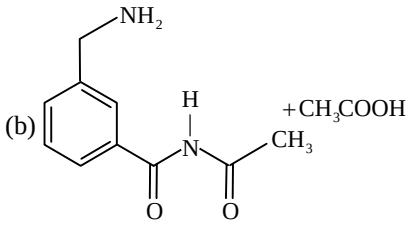
   the structure of the Product T is
   (a) 
   (b) 
   (c) 
   (d) 

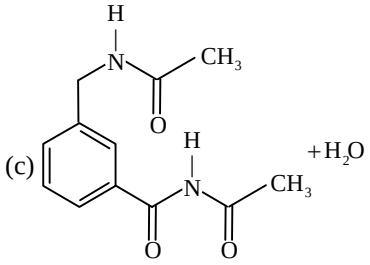
3. A compound with molecular mass 180 is acylated with CH_3COCl to get a compound with molecular mass 390. The number of amino groups present per molecule of the former compound is
   (a) 2 (b) 5
   (c) 4 (d) 6

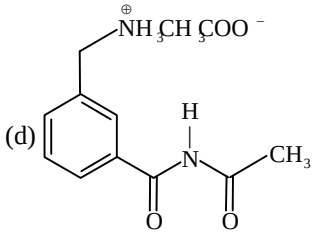
4. The gas leaked from a storage tank of the Union Carbide plant in Bhopal gas tragedy was
   (a) Methylisocyanate
   (b) Methylamine
   (c) Ammonia
   (d) Phosgene

5. In the reaction shown below, the major product(s) formed is/are


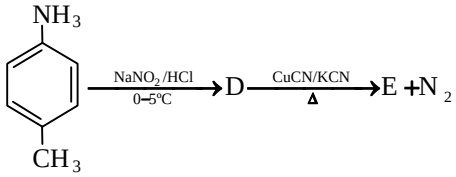
   (a) 

   (b) 

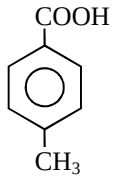
   (c) 

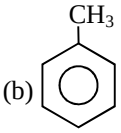
   (d) 

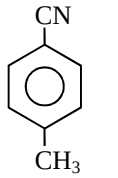
6. For the identification of **β –** naphthol using dye test, it is necessary to use
   (a) dichloromethane solution of β- naphthol
   (b) acidic solution of β- naphthol
   (c) neutral solution of β- naphthol
   (d) alkaline solution of β- naphthol

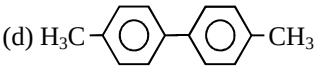
7. In the reaction 

   The product E is

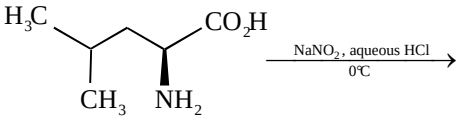
(a) 

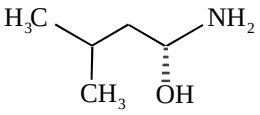
(b) 

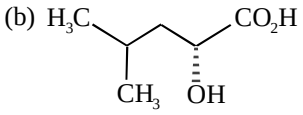
(c) 

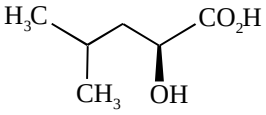
(d) 

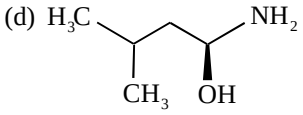
8. The major product of the reaction is



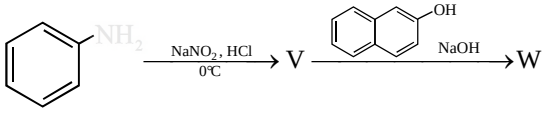
(a) 

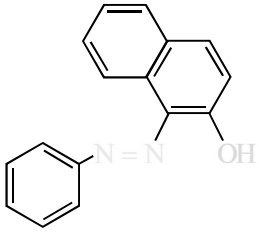
(b) 

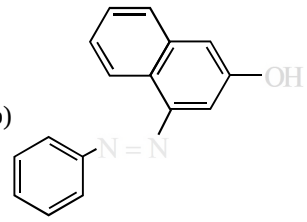
(c) 

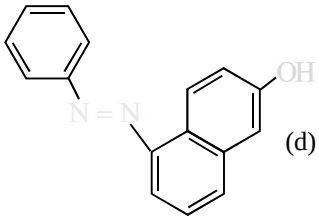
(d) 

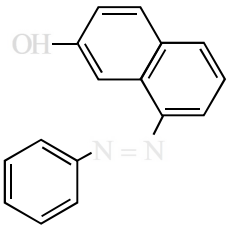
9. In the following reactions, the major product W is



(a) 

(b) 

(c) 

(d) 

10. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are:

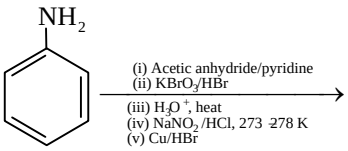
(a) One mole of NaOH and one mole of Br_2

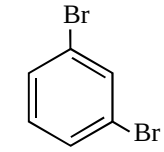
(b) Four moles of NaOH and two moles of Br_2

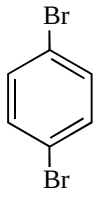
(c) Two moles of NaOH and two moles of Br_2

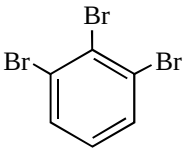
(d) Four moles of NaOH and one mole of Br_2

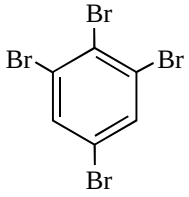
11. The product(s) of the following reaction sequence is (are)



(a) 

(b) 

(c) 

(d) 

12. The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}

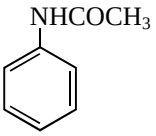
(a) can also be prepared by reaction of P_4 and HNO_3

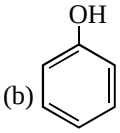
(b) is diamagnetic

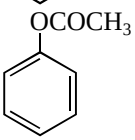
(c) contains one N-N bond

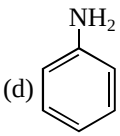
(d) reacts with Na metal producing a brown gas

13. Which of the following compounds will form significant amount of meta product during mono - nitration reaction?

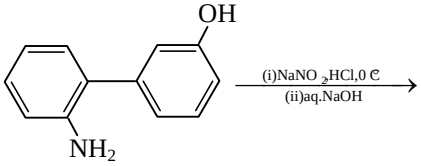
(a) 

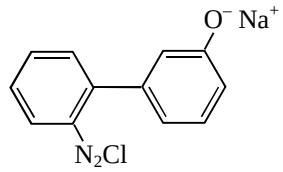
(b) 

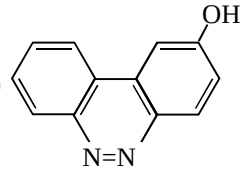
(c) 

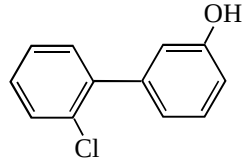
(d) 

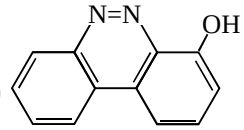
14. The major product of the following reactions is



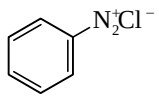
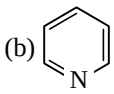
(a) 

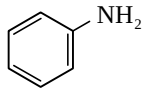
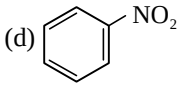
(b) 

(c) 

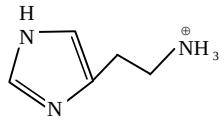
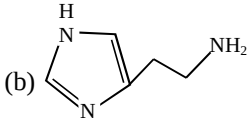
(d) 

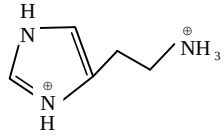
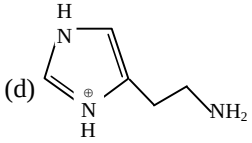
15. Which of the following compounds will be suitable for Kjeldahl's method for nitrogen estimation?

(a)  (b) 

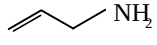
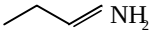
(c)  (d) 

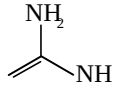
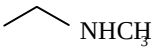
16. The predominate form of histamine present in human blood is (pK_a, Histidine = 6.0)

(a)  (b) 

(c)  (d) 

17. The increasing order of basicity of the following compound

(a)  (b) 

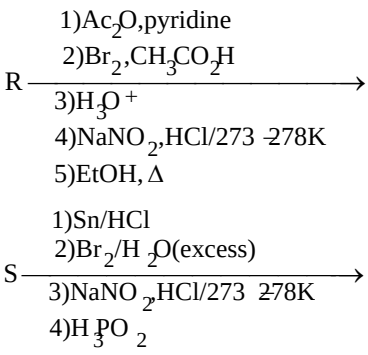
(c)  (d) 

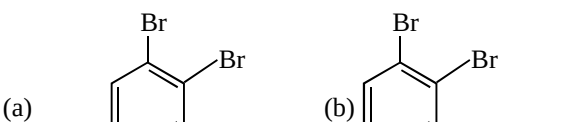
(a) (d) < (b) < (a) < (c)
(b) (a) < (b) < (c) < (d)
(c) (b) < (a) < (c) < (d)
(d) (b) < (a) < (d) < (c)

18. The compound that does not produce nitrogen gas by the thermal decomposition is
(a) $(NH_4)_2SO_4$ (b) $Ba(N_3)_2$
(c) $(NH_4)_2Cr_2O_7$ (d) NH_4NO_2

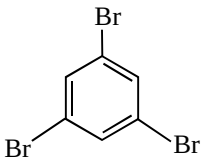
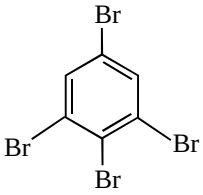
19. The compound(s) which generate(s) N_2 gas upon thermal decomposition below 300°C is (are)
(a) NH_4NO_3 (b) $(NH_4)_2Cr_2O_7$
(c) $Ba(N_3)_2$ (d) Mg_3N_2

20. Aniline reacts with mixed acid (conc. HNO_3 and conc. H_2SO_4) at 288 K to give P (51 %), Q (47%) and R (2%). The major product(s) of the following reaction sequence is (are)

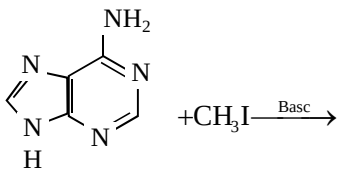


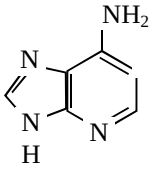
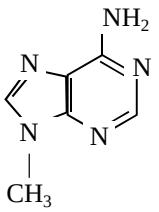


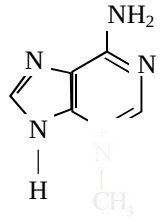
(a) (b)

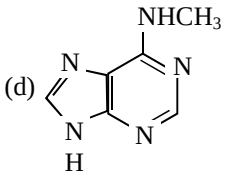
(c)  (d) 

21. The major product in the following reaction is:

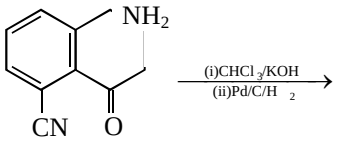


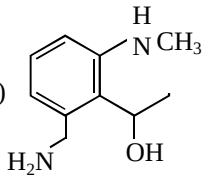
(a)  (b) 

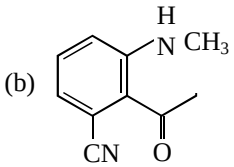
(c) 

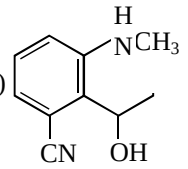
(d) 

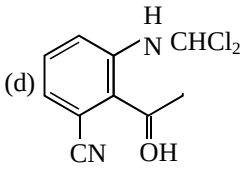
22. The major product obtained in the following reaction is:



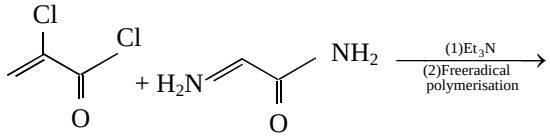
(a) 

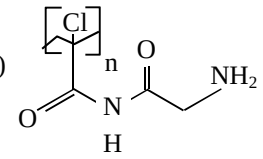
(b) 

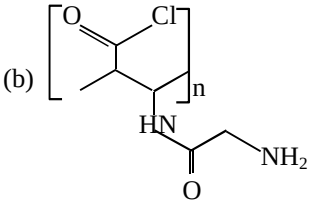
(c) 

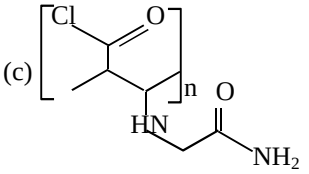
(d) 

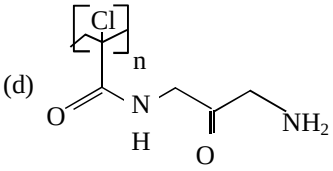
23. Major product of the following reaction is:



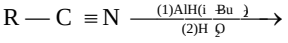
(a) 

(b) 

(c) 

(d) 

24. The major product of following reaction is:



(a) RCHO

(b) RCOOH

(c) RCH_2NH_2

(d) $RCONH_2$

25. The increasing order of pKa of the following amino acids in aqueous solution is:

Gly Asp Lys Arg

(a) Asp < Gly < Arg < Lys

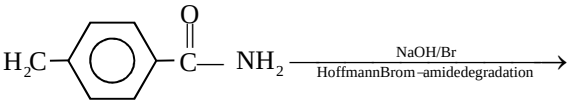
(b) Arg < Lys < Gly < Asp

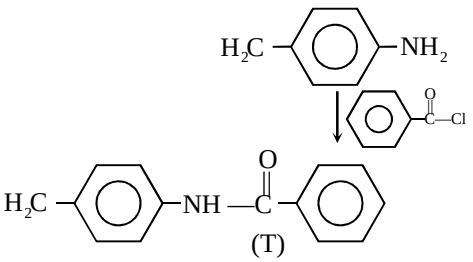
(c) Gly < Asp < Arg < Lys

(d) Asp < Gly < Lys < Arg

ANSWERS and SOLUTIONS

1. (d) Isocyanide test/Carbylamine reaction

2. (c) 

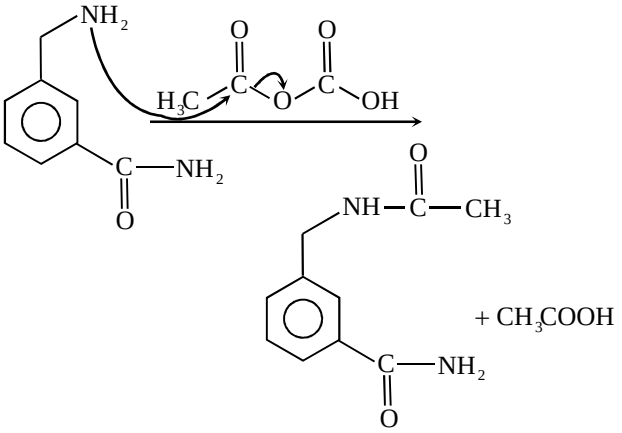


(T)

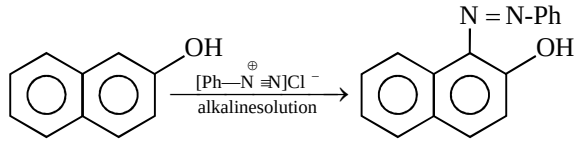
3. (b) No. of amino group $= \frac{390-180}{42} = 5$

4. (a) Factual

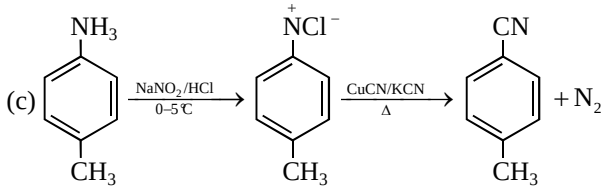
5. (a) Only amines undergo acetylation and not acid amides.



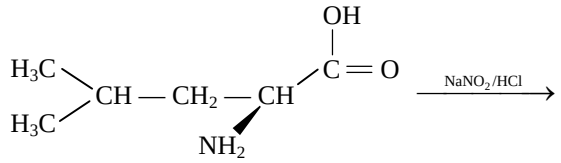
6. (d)

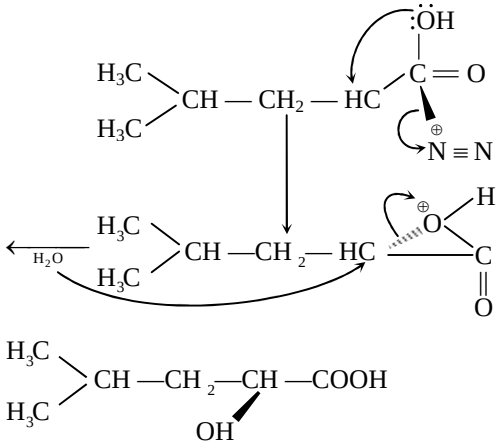


7. (c)

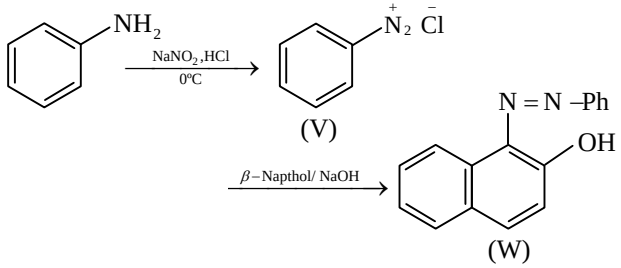


8. (c)

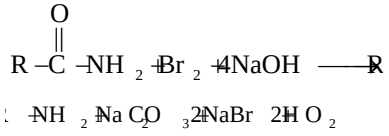




9. (a)

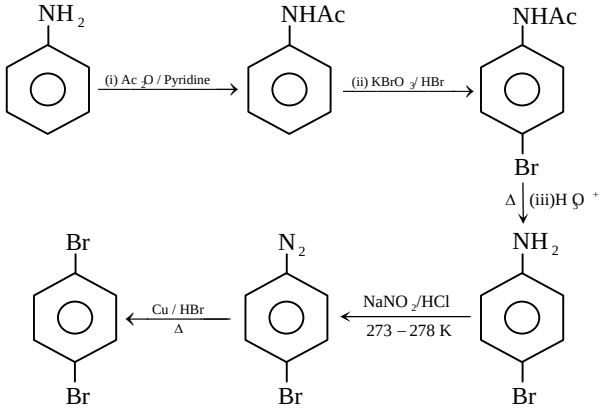


10. (d) Hofmann bromamide degradation reaction



1 mole of bromine and 4 moles of NaOH are used for per mole of amine produced.

11. (b)



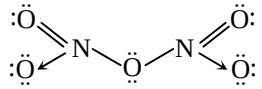
12. (b, d) $4HNO_3 + P_4O_{10} \longrightarrow 2N_2O_5 + 4HPO_3$

So, nitrogen containing compound is N_2O_5.

(A) $P_4 + 20HNO_3 \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$

N_2O_5 can't be prepared by reaction of P_4 & HNO_3.

(B) N_2O_5 is diamagnetic.

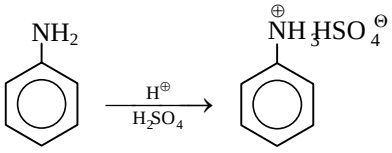


(C) Structure of N_2O_5 is (It does not contain N – N bond)

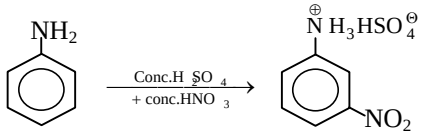
(D) $N_2O_5 + Na \longrightarrow NaNO_3 + NO_2 \uparrow$

13. (d) (i) Nitration is carried out in presence of concentrated HNO_3 + concentrated H_2SO_4.

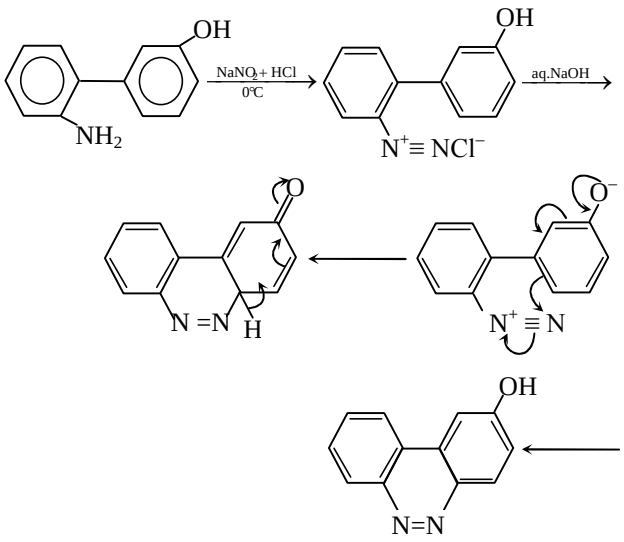
(ii) Aniline acts as base. In presence of H_2SO_4 its protonation takes place and anilinium ion is formed.



(iii) Anilinium ion is strongly deactivating group and meta directing in nature so it give meta nitration product in significant amount.

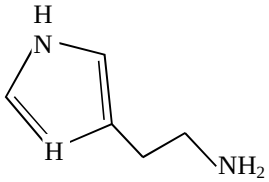


14. (b)

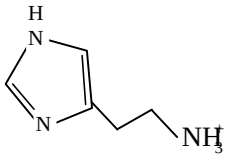


15. (c) Kjeldahl's method is not applicable for compounds containing nitrogen in nitro, and azo groups and nitrogen in ring, as N of these compounds does not change to ammonium sulphate under these conditions. Hence only aniline can be used for estimation of nitrogen by Kjeldahl's method.

16. (a) Histamine



At pH (7.4) major form of histamine is protonated at primary amine.

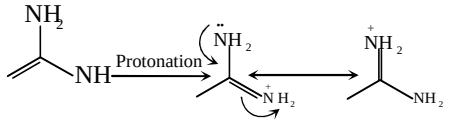


17. (d)

(a) NH_2 Protonation $\overset{+}{N}H_3$ 1° &sp^3

(b) NH Protonation $\overset{+}{N}H_2$ sp^2

(c) NH_2 Protonation



(d) $NHCH_3$ Protonation $\overset{+}{N}H_2-CH_3$ 2° &sp^3

∴ Correct order of basicity

18. (a) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

$NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$

$(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_3 + H_2SO_4$

$Ba(N_2)_2 \xrightarrow{\Delta} Ba + 3N_2$

Among all the given compounds, only $(NH_4)_2SO_4$ do not form dinitrogen on heating, it produces ammonia gas.

19. (b, c) NH_4NO_3 on heating at 250ºC decomposes to Nitrous oxide and water.

$$NH_4NO_3 \longrightarrow N_2O + H_2O$$

Nitrous oxide above 600°C decomposes to dinitrogen and dioxygen gas.

$$2N_2O \longrightarrow 2N_2 + O_2$$

Ammonium dichromate on heating decomposes to give dinitrogen and chromium (III) oxide.

$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

Barium azide on heating around 180°C decomposes to give dinitrogen gas and barium.

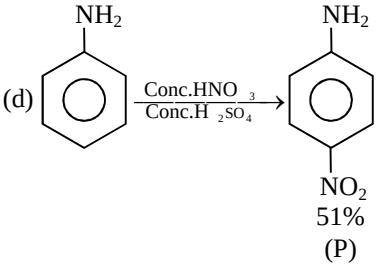
$$Ba(N_3)_2 \longrightarrow 3N_2 + Ba$$

Magnesium nitride decomposes above 700°C to give magnesium and dinitrogen gas.

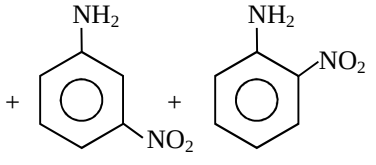
$$Mg_3N_2 \longrightarrow 3Mg + N_2$$

So below 300°C only $(NH_4)_2Cr_2O_7$ and $Ba(N_3)_2$ can provide N_2 gas on heating

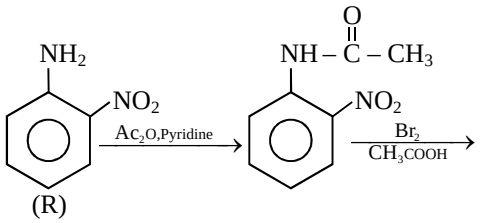
20. (d)



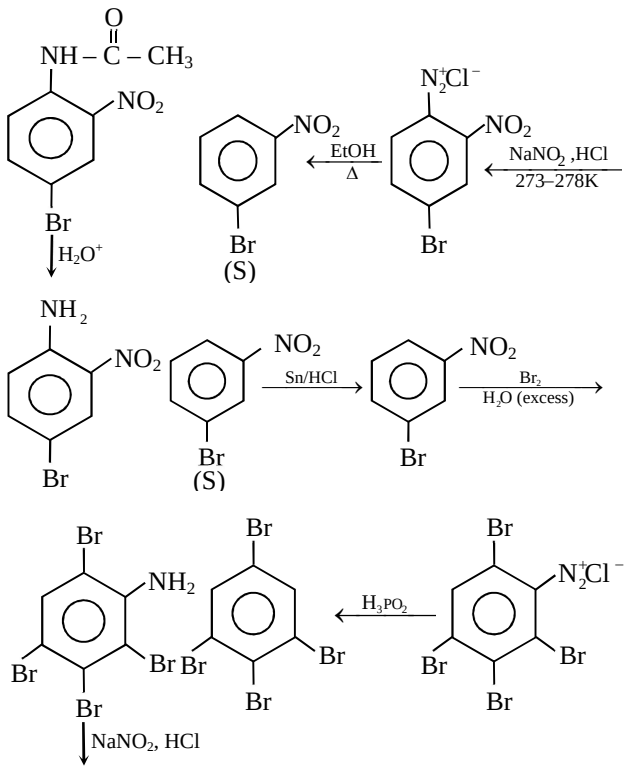
51%
(P)



47% 2%
(Q) (R)

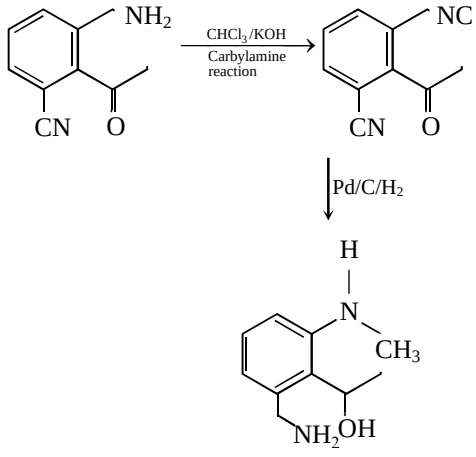


(R)

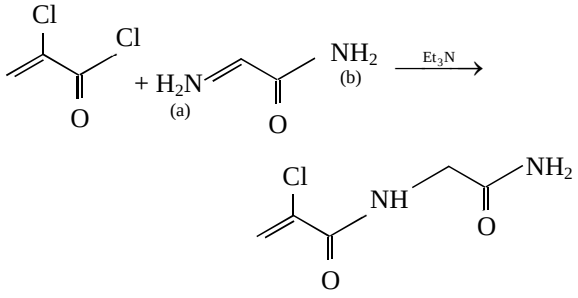


21. (b) Because one double bond is missing in all the given options. So aromaticity is lost in both the rings.

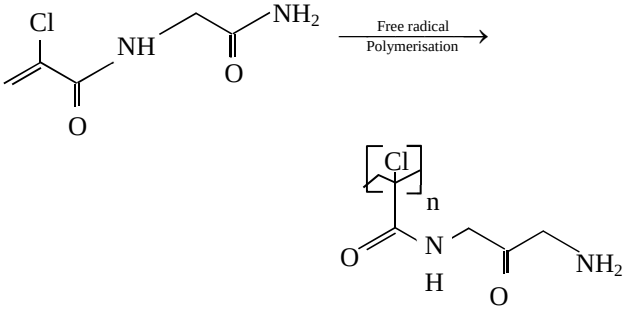
22. (a)



23. (d)

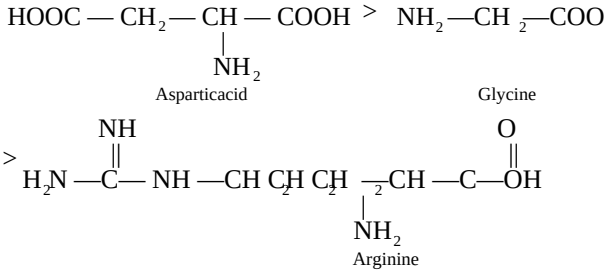


NH_2 (a) will act as nucleophile as (b) is having delocalised lone pair.



24. (a) $R—C \equiv N \xrightarrow{AlH(i\text{–}Bu)_2} R—C=N \xrightarrow{H_2O} R—C=N$

25. (d) Order of acidic strength:



So pK_a

Asp < Gly < Lys < Arg

❑❑❑