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AMINES

NITROGEN CONTAINING COMPOUNDS

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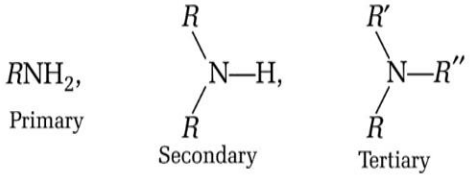
CHEMISTRY
IIT-NEET

AMINES
NITROGEN CONTAINING COMPOUNDS

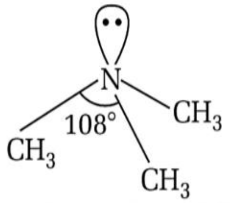
- Amines
- Diazonium Salts

Amines

These are the derivatives of ammonia in which one, two or all the three hydrogen atoms are replaced by alkyl or aryl groups. Amines are classified as primary, secondary and tertiary according to the replacement of one, two or three hydrogen atoms from ammonia respectively.

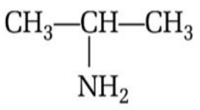


- Nitrogen, in amines, contains four sp^3-hybridised orbitals. Out of these four, the three sp^3-hybridised orbitals of nitrogen overlap either with s-orbitals of hydrogen or sp^3- orbitals carbon depending upon the composition of amines. The fourth hybridised orbital of nitrogen in all amines has unshared pair of electrons.
  Due to the presence of lone pair of electrons, lone pair-bond pair repulsions increases due to which the bond angle C—N—E of nomenclature (where, E is C or H) 109.5° and shape is pyramidal.



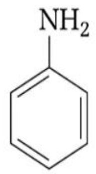
Pyramidal shape of trimethylamine

- In common system of nomenclature, an aliphatic amine is named by prefixing alkyl group to amine, i.e. alkylamine. In **IUPAC system**, amines are named as alkanamines, derived by replacement of 'e' of alkane by the word amine. While naming arylamine suffix 'e' of arene is replaced by 'amine'.



$CH_3—\underset{\displaystyle NH_2}{\underset{|}{CH}}—CH_3$

Propan-2-amine

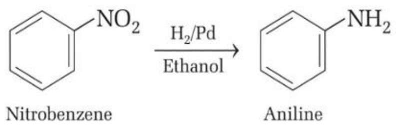


Benzenamine

Preparation of Amines

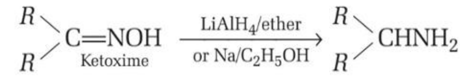
Several methods can be used to prepare aliphatic amines, out of which some are specific for 1°, 2°, 3° amines while some gives mixtures of all the three. These are as follows:

(i) Alkyl nitriles, nitroalkanes, oximes of aldehydes, ketones and amides, all on reduction give primary amines. Reduction of nitriles to primary amines by using Na and alcohol is called **Mendius reaction**.

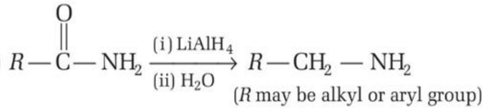
(a)


(b) $R—NO_2 \xrightarrow[\text{or Fe +HCl}]{\text{Sn +HCl}} \underset{\text{Primary amine}}{R—NH_2}$

(c) $R—C\equiv N \xrightarrow[Na(Hg)\ /\ C_2H_5OH]{H_2/Ni} R—CH_2—NH_2$

(d)


$$\begin{matrix}R\\R\end{matrix}\!\!>\underset{\text{Ketoxime}}{C{=}NOH} \xrightarrow[\text{or } Na/C_2H_5OH]{LiAlH_4/\text{ether}} \begin{matrix}R\\R\end{matrix}\!\!>CHNH_2$$

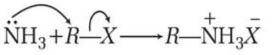
(e)


$$R—\overset{\overset{\Large O}{||}}{C}—NH_2 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } LiAlH_4} R—CH_2—NH_2$$

(R may be alkyl or aryl group)

NOTE $\underset{\text{Isocyanide}}{R—N\equiv C} \xrightarrow[\text{or Na (Hg)} + C_2H_5OH]{H_2/Ni} \underset{(2°\ \text{amine})}{R—NH—CH_3}$

(ii) When alkyl halide is heated with alcoholic solution of ammonia in a sealed tube at about 393 K, a mixture of amines is obtained. This reaction is called **Hofmann's ammonolysis method.**



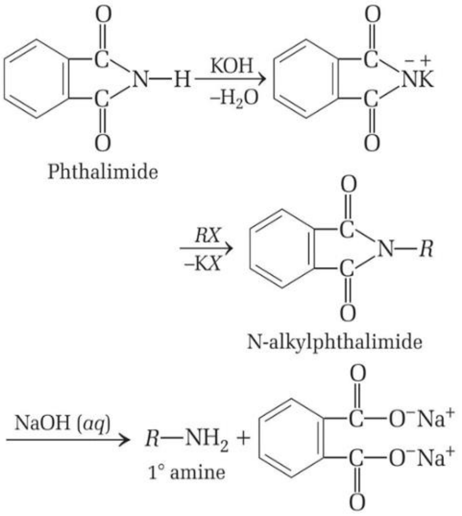
$$\ddot{N}H_3 + R—X \longrightarrow R—\overset{+}{N}H_3\overset{-}{X}$$

$$\underset{1°}{RNH_2} \xrightarrow{RX} \underset{2°}{R_2NH} \xrightarrow{RX} \underset{3°}{R_2N} \xrightarrow{RX} \underset{\text{Quaternary ammonium salt}}{R_4\overset{+}{N}\overset{-}{X}}$$

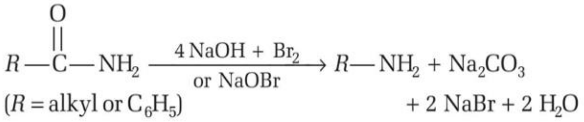
The free amine can be obtained from ammonium salt by treatment with a strong base.

$$R\overset{+}{N}H_3X^- + NaOH \longrightarrow R—NH_2 + H_2O + Na^+X^-$$

(iii) **Gabriel phthalimide synthesis** is used for the preparation of 1° amine. In this reaction, phthalimide on treatment with ethanolic KOH forms potassium salt of phthalimide which on heating with RX followed by either alkaline hydrolysis or hydrazinolysis with hydrazine ($H_2N \cdot NH_2$) produces the corresponding 1° amine. Primary aromatic amine (except those containing electron withdrawing group at *o*- and *p*-positions, e.g. $—NO_2$ group) cannot be synthesised by this method because ArX do not undergo S_N reaction with anion formed by phthalimide.



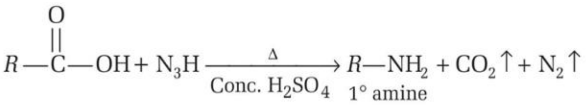
(iv) Amides on reaction with Br_2 in an aqueous or ethanolic solution of NaOH give 1° amine with one C-atom less than that present in the amide. This reaction is called **Hofmann-Bromamide degradation reaction.**



$$R—\overset{\overset{\Large O}{||}}{C}—NH_2 \xrightarrow[\text{or NaOBr}]{4\,NaOH + Br_2} R—NH_2 + Na_2CO_3 + 2\,NaBr + 2\,H_2O$$

(R = alkyl or C_6H_5)

(v) Carboxylic acid, when warmed with hydrazoic acid (N_3H) in the presence of concentrated sulphuric acid, gives a high yield of primary amines. This reaction is called **Schmidt reaction**.



$$R—\overset{\overset{\Large O}{||}}{C}—OH + N_3H \xrightarrow[\text{Conc. } H_2SO_4]{\Delta} \underset{1°\ \text{amine}}{R—NH_2} + CO_2\uparrow + N_2\uparrow$$

Instead of N_3H and conc. H_2SO_4, a mixture of NaN_3 and conc. H_2SO_4 can also be used.

Physical Properties

Some important physical properties of amines are discussed below :

- The lower aliphatic amines are gases with fishy odour. Aniline and other arylamines are usually colourless but develop colour on keeping it in air for a long time due to atmospheric oxidation.
- Boiling points and solubility of isomeric amines decrease with branching, i.e.

$$\underset{\substack{1°\ \text{amine}\\(2\,\text{H-bonding})}}{CH_3—CH_2—CH_2—NH_2} > \underset{\substack{2°\ \text{amine}\\(1\,\text{H-bonding})}}{CH_3—NH—CH_2—CH_3} > \underset{\substack{3°\ \text{amine}\\(\text{No H-bonding})}}{(CH_3)_3N}$$

- Amines have lower boiling point than corresponding alcohols.

Chemical Properties

Amines are reactive and behave as nucleophiles due to the presence of one unshared pair of electrons. Some important chemical properties of amines are discussed below:

1. Basic Nature of Amines

- Amines are basic in nature, so react with acids and form salt. Larger the value of K_b or smaller the value of pK_b, stronger is the base.

  In RNH_2, $RN{=}CHR$ and RCN, nitrogen is sp^3, sp^2 and sp-hybridised respectively. More the s-character of hybridised orbital containing lone pair, lesser is the basic character. Hence, RNH_2 is most basic and RCN is least basic among these.
- The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

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

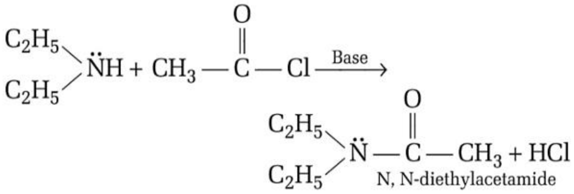
  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- Electron donating substituent such as $-CH_3$, $-OCH_3$ increases the basicity while electron withdrawing group such as $-NO_2$, $-COOH$ decreases the basicity.

NOTE In gaseous phase, the order of basicity would be 3° amine > 2° amine > 1° amine > NH_3.

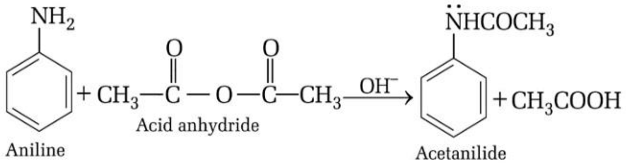
2. Acylation

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydride and esters by nucleophilic substitution reaction. This reaction is known as acylation. In this reaction, 1° amines give N-substituted amide, while 2° amines give N,N-disubstituted amides.

$$C_2H_5{-}NH_2 + \underset{\text{(Acyl chloride)}}{CH_3COCl} \xrightarrow{OH^-} \underset{\text{N-ethylethanamide}}{C_2H_5{-}NHCOCH_3} + HCl$$



$$(C_2H_5)_2\ddot{N}H + CH_3{-}\overset{O}{\overset{\|}{C}}{-}Cl \xrightarrow{Base} \underset{\text{N, N-diethylacetamide}}{(C_2H_5)_2\ddot{N}{-}\overset{O}{\overset{\|}{C}}{-}CH_3} + HCl$$



3. Carbylamine Reaction

Aliphatic and aromatic primary amines on heating with $CHCl_3$ and KOH(alc.) form isocyanide or carbylamine which is a foul smelling substance. Secondary ($R{-}NH{-}R$) and tertiary amines (R_3N) do not show this reaction. This reaction is known as carbylamine reaction and it is used as a test for primary amines.

$$R{-}NH_2 + CHCl_3 + 3KOH(alc.) \xrightarrow{\Delta} \underset{\text{Carbylamine}}{R{-}NC} + 3KCl + 3H_2O$$

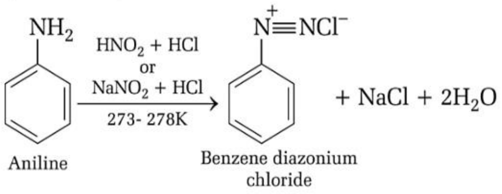
4. Reaction with Nitrous Acid

Primary, secondary and tertiary amines react differently with nitrous acid which is prepared *in situ* from a mineral acid and sodium nitrite.

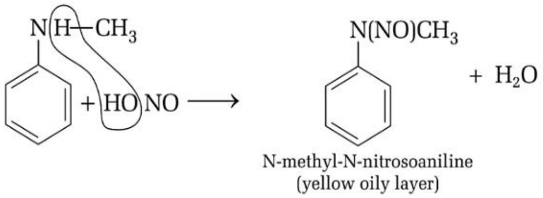
(i) Aliphatic primary amines when react with HNO_2, gives alcohol.

$$R{-}NH_2 \xrightarrow[NaNO_2 + HCl]{(HNO_2)} [R\overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2\uparrow + HCl$$

(ii) Aromatic primary amines when react with HNO_2 at low temperatures, give diazonium salts.



(iii) Secondary amines both aliphatic and aromatic on reaction with HNO_2 give an oily nitroso compound.



(iv) Tertiary aliphatic amines dissolve in a cold solution of nitrous acid to form water soluble nitrite salts which decompose on warming to give nitrosoamine and alcohol.

$$\underset{3^\circ\text{ amine}}{(C_2H_5)_3N} + HONO \xrightarrow{Cold} \underset{\text{Trimethylammonium nitrite salt}}{[(C_2H_5)_3N^+H]\,NO_2^-}$$

$$\xrightarrow{Warm} (C_2H_5)_2N{-}N{=}O + C_2H_5OH$$

(v) Aromatic amines react with nitrous acid to form aliphatic diazonium salts at low temperatures (273-278 K).

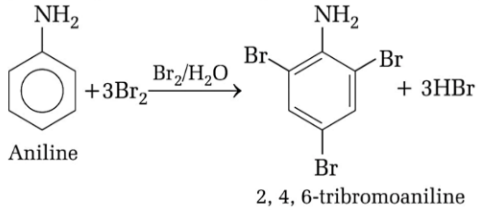
$C_6H_5{-}NH_2 \xrightarrow[273–278\,K]{NaNO_2 + 2HCl} C_6H_5{-}\overset{+}{N_2}\overset{-}{Cl} + NaCl + 2H_2O$ This reaction is used to distinguish 1°, 2° and 3° amines.

5. Electrophilic Substitution Reaction

In electrophilic substitution reaction, an atom that is attached to an aromatic system is replaced by an electrophile. In case of aniline, $-NH_2$ group is *ortho* and *para* directing and a powerful activating group. These positions become the centre of high electron density.

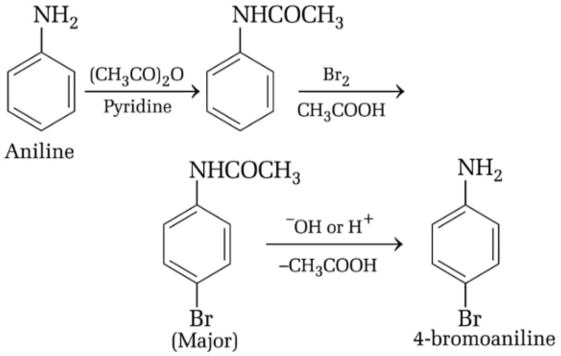
Some of the most important electrophilic aromatic substitution, i.e. bromination, nitration, sulphonation etc., are given below:

(i) Due to strong activating effect of the amino group, halogenation (or bromination) of amines occur very fast.

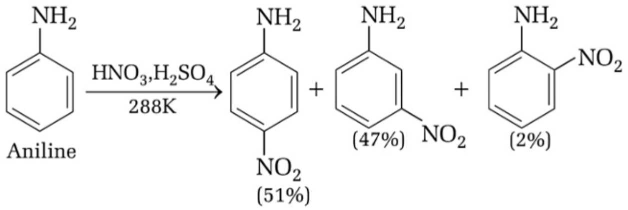


The main problem encountered during electrophilic substitution reactions of aromatic amines is that these have very high reactivity.

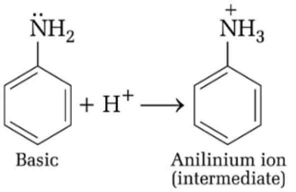
A monohalogenated (or monobrominated) product can be obtained by selective bromination. This can be done by protecting the —NH_2 group by acetylation with acetic anhydride then carrying out the desired substitution followed by hydrolysis of amide.



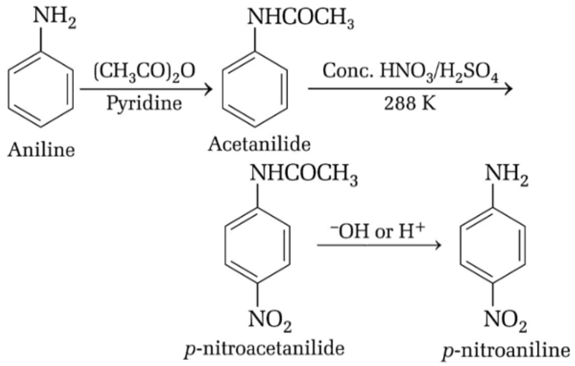
(ii) Aniline can be treated with nitric acid and sulphuric acid to give nitrobenzene *via* nitration process.



This is due to the fact that aniline gets protonated to form anilinium ion which is *meta*-directing.

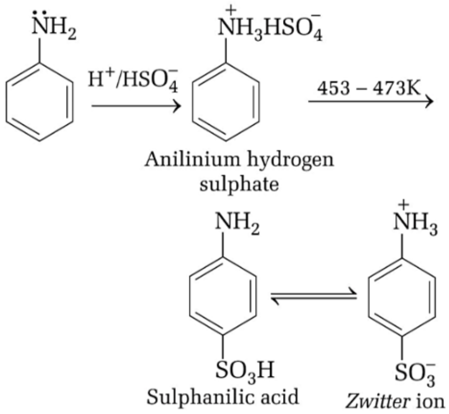


By protecting the —NH_2 group through acetylation with acetic anhydride, the nitration can be controlled and *p*-nitroaniline is obtained as a major product.



Aniline does not undergo Friedel-Craft's reaction (alkylation and acetylation) due to salt formation with $AlCl_3$ (anhy.), a Lewis acid, which is used as a catalyst.

(iii) Aniline can be treated with a conc. H_2SO_4 to give anilinium hydrogen sulphate which on heating with sulphuric acid at 453-473 K produces sulphanilic acid in a reversible reaction *via* sulphonation.



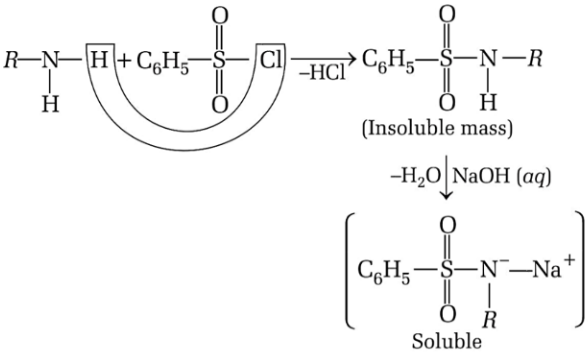
Identification of 1°, 2° and 3° Amines

Several reactions can be used to identify 1°, 2° and 3° amines. Some important test are as follows:

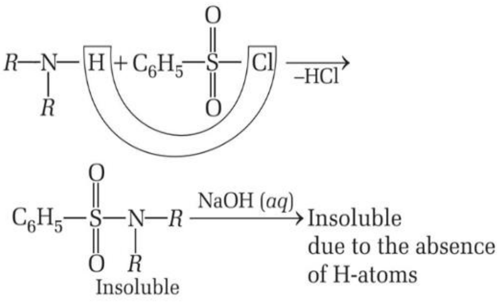
Hinsberg's Test

Distinction between primary, secondary and tertiary amines is made by $C_6H_5SO_2Cl$, which is known as Hinsberg's reagent.

(i) **Primary amines** give an insoluble mass which is soluble in alkali.



(ii) **Secondary amines** give an insoluble substance, which remains unaffected by alkali.



(iii) **Tertiary amines** do not react with benzene sulphonyl chloride because of the absence of replaceable H-atoms on N-atom.

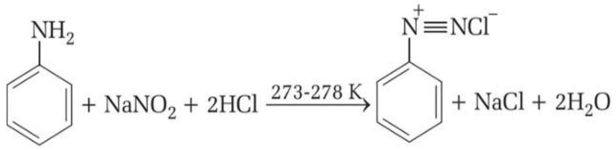
Carbylamine reaction and reaction with nitrous acid can also be used to distinguish between 1°, 2° and 3° amines as discussed before in this chapter.

Uses of Amines

Amines are used as intermediates in drug manufacturing and as reagents in organic synthesis. Aromatic amines are used for manufacture of polymers, dyes and as intermediates for additives in rubber industry. Quaternary ammonium salts of long chain aliphatic tertiary amines are used as detergents.

Diazonium Salts

- Diazonium salts are obtained when primary aromatic amines react with nitrous acid. These salts are used in the preparation of azo dyes and a number of useful halogen substituted arenes.
- Benzene diazonium chloride is prepared by the reaction of aniline with nitrous acid at 273-278 K. The conversion of primary aromatic amines into diazonium salt is known as diazotisation.



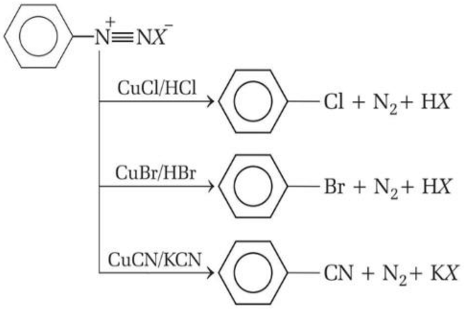
- Benzene diazonium chloride is a colourless crystalline solid. It is readily soluble in water. It is stable in cold but reacts with water when warmed.

Diazonium salts mainly show two types of reactions. These are as follows:

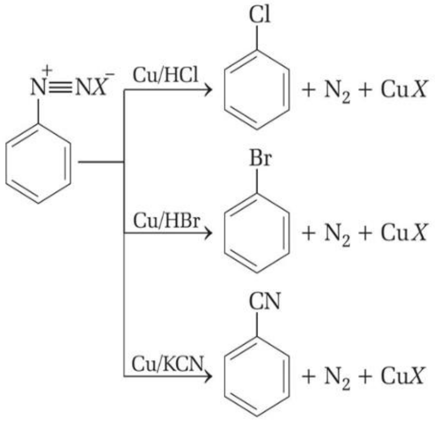
1. Reactions Involving Displacement of Diazo Group

The following reactions are involved in the displacement of diazo group in the benzene can be given as :

(i) Benzene diazonium chloride heated with cuprous chloride or bromide respectively dissolved in HCl or HBr yield chlorobenzene or bromobenzene, respectively. This reaction is called **Sandmeyer's reaction.**



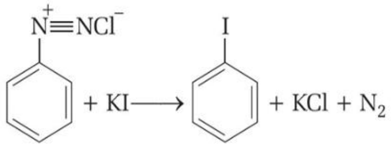
(ii) In **Gattermann reaction**, benzene diazonium chloride is warmed with copper powder and HCl, HBr and KCN to produce chlorobenzene, bromobenzene and cyanobenzene respectively.



The yield in Sandmeyer's reaction is found to be greater than the Gattermann reaction.

(iii) Some other reactions of diazonium salt involving displacement of diazo group.

(a)



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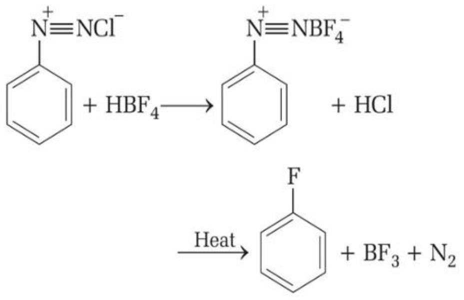
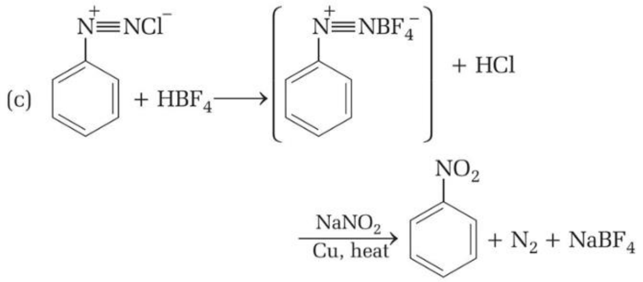
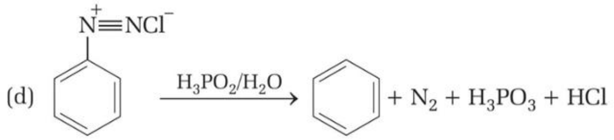
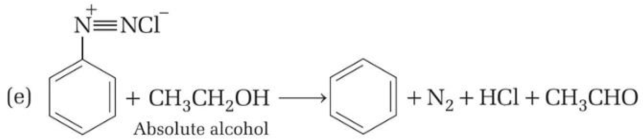
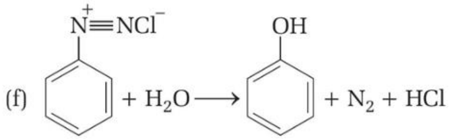






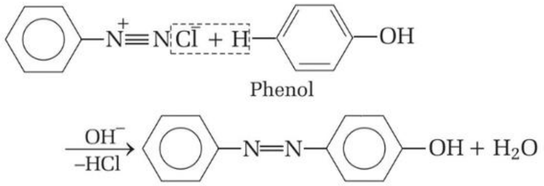




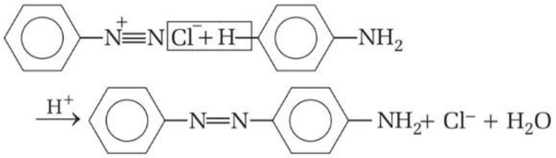
2. Reactions Involving Retention of Diazo Group

Coupling reactions are the example of electrophilic substitution reaction.

The azo products obtained have an extended conjugate system having both the aromatic rings joined through the —N = N— bond.



p-hydroxyazobenzene (Orange dye)



p-aminoazobenzene (Yellow dye)

Coupling with phenols is carried out in weakly alkaline medium (pH 9 to 10) because phenolate ion produced is coupled with diazonium salt more readily. Above pH 10, diazonium salt reacts with hydroxide ion to form diazotate ion which does not take part in coupling reaction.

Uses of Diazonium Salts

Diazonium salts are used for the preparation of a large number of aromatic compounds *viz* substitution and coupling compounds.

FOUNDATION QUESTIONS EXERCISE

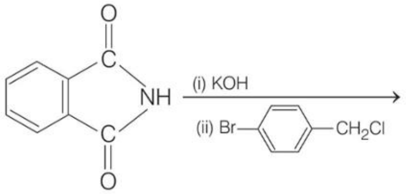
1 Reduction of aromatic nitro compounds using Fe and HCl gives

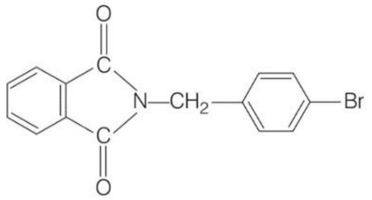
(a) aromatic oxime (b) aromatic hydrocarbon
(c) aromatic primary amine (d) aromatic amide

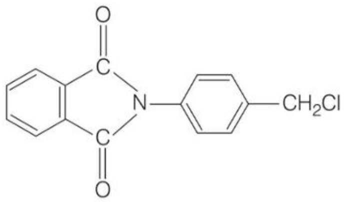
2 In which of the following reaction, tertiary amine is obtained?

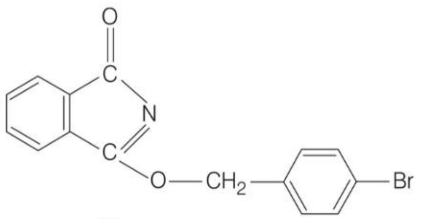
(a) Aniline $\xrightarrow{CH_3I}\xrightarrow{CH_3I}$ (b) Aniline $\xrightarrow{CH_3I}$
(c) Nitrobenzene $\xrightarrow{Sn/HCl}$ (d) None of these

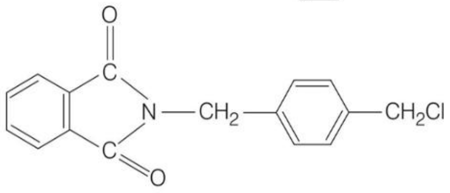
3 The major product of the following reaction is



(a)


(b)


(c) 

(d) 

4 The best reagent for converting 2-phenylpropanamide into 2-phenylpropanamine is

(a) excess H_2
(b) Br_2 in aqueous NaOH
(c) iodine in the presence of phosphorus
(d) $LiAlH_4$ in ether

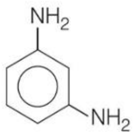
5 Acetamide is treated separately with the following reagents. Which one of these would give methylamine?

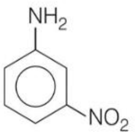
(a) PCl_5
(b) $NaOH + Br_2$
(c) Soda lime
(d) Hot conc. H_2SO_4

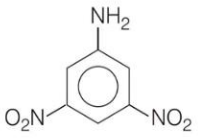
6 In the Hofmann-bromamide degradation reaction, the number of moles of NaOH and Br_2 used per mole of amine produced are → JEE Main 2016

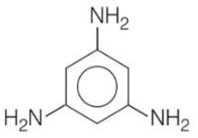
(a) four moles of NaOH and two moles of Br_2
(b) two moles of NaOH and two moles of Br_2
(c) four moles of NaOH and one mole of Br_2
(d) one mole of NaOH and two moles of Br_2

7 The major product of the reaction between *m*-dinitrobenzene and NH_4SH is

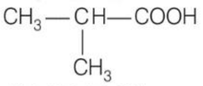
(a) 

(b) 

(c) 

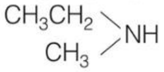
(d) 

8 An organic compound *A* on reacting with NH_3 gives *B*. On heating, *B* gives *C*. *C* in the presence of KOH reacts with Br_2 to give $CH_3CH_2NH_2$. *A* is → Online JEE Main 2013

(a) CH_3COOH
(b) $CH_3CH_2CH_2COOH$
(c) 
$CH_3-\underset{\substack{|\\CH_3}}{CH}-COOH$
(d) CH_3CH_2COOH

9 Which of the following should be most volatile?

I. $CH_3CH_2CH_2NH_2$ II. $(CH_3)_3N$

III. 

IV. $CH_3CH_2CH_3$

(a) II (b) IV (c) I (d) III

10 Amongst the following, the strongest base in aqueous medium is

(a) CH_3NH_2 (b) $NCCH_2NH_2$
(c) $(CH_3)_2NH$ (d) $C_6H_5NHCH_3$

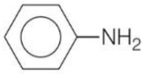
11. Which one of the following is the strongest base in aqueous solution?

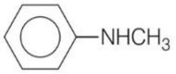
(a) Trimethyl amine (b) Aniline
(c) Dimethyl amine (d) Methyl amine

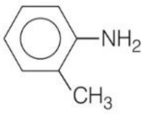
12. The order of basicity of amines in gaseous state is → JEE Main (Online) 2013

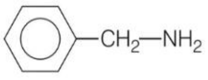
(a) 1°> 2°> 3°> NH_3 (b) 3°> 2°> NH_3 > 1°
(c) 3°> 2°> 1°> NH_3 (d) NH_3 > 1°> 2°> 3°

13. Which of the following is the strongest base?

(a) 

(b) 

(c) 

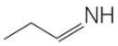
(d) 

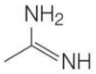
14. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? → JEE Main 2014

(a) $(CH_3)_2NH$ (b) CH_3NH_2
(c) $(CH_3)_3N$ (d) $C_6H_5NH_2$

15. The increasing order of basicity of the following compounds is

I. 

II. 

III. 

IV. 

(a) I < II < III < IV (b) II < I < III < IV
(c) II < I < IV < III (d) IV < II < I < III

16 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 → JEE Main (Online) 2013

(a) 2 (b) 5
(c) 4 (d) 6

17 On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is → JEE Main 2014

(a) an alkanol (b) an alkanediol
(c) an alkyl cyanide (d) an alkyl isocyanide

18 Carbylamine forms from aliphatic or aromatic primary amine *via* which of the following intermediates?
➞ JEE Main (Online) 2013

(a) Carbanion (b) Carbene
(c) Carbocation (d) Carbon radical

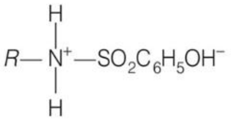
19 Which of the following is formed when $R\,NH_2$ reacts with $R\,CHO$?

(a) Hemiacetals (b) Acetals
(c) Ketals (d) Imines

20 The compound, which on reaction with aqueous nitrous acid at low temperature, produces an oily nitrosoamine, is

(a) diethylamine (b) ethylamine
(c) aniline (d) methyl amine

21 $R\,NH_2$ reacts with $C_6H_5SO_2Cl$ in aqueous KOH to give a clear solution. On acidification a precipitate is obtained which is due to the formation of

(a) 
$R—\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{N^+}}—SO_2C_6H_5OH^-$
(b) $R—N^-SO_2C_6H_5K^+$

(c) $C_6H_5SO_2NH_2$ (d) $R—NH—SO_2—C_6H_5$

22 Which one of the following methods is neither meant for the synthesis nor for separation of amines?

(a) Curtius reaction (b) Wurtz reaction
(c) Hofmann method (d) Hinsberg method

23 Match the following and choose the correct option.

Column I	Column II
A. Ammonolysis	1. Amine with lesser number of carbon atoms
B. Gabriel phthalimide synthesis	2. Detection test for primary amines
C. Hofmann bromamide reaction	3. Reaction of phthalimide with KOH and $R—X$
D. Carbylamine reaction	4. Reaction of alkyl halides with NH_3

Codes

	A	B	C	D		A	B	C	D
(a)	2	1	3	4	(b)	4	3	1	2
(c)	3	2	4	1	(d)	4	1	3	2

24 On heating aniline with fuming sulphuric acid at 180°C, the compound formed will be

(a) aniline disulphate (b) aniline-2,4,6-trisulphonic acid
(c) sulphanilic acid (d) None of these

25 Nitration of aniline also gives *m*-nitroaniline in strong acidic medium because

(a) in electrophilic substitution reaction amino group is *meta*-directive
(b) inspite of substituents nitro group always goes to *m* -position
(c) in acidic (strong) medium aniline is present as anilinium ion
(d) None of the above

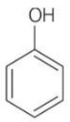
26 Which of the following will give only one monosubstituted product?

(a) *o*-dinitrobenzene (b) *m*-dinitrobenzene
(c) *p*-dinitrobenzene (d) None of these

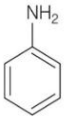
27 Acetanilide on nitration followed by alkaline hydrolysis mainly gives

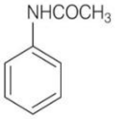
(a) *o*-nitroacetanilide (b) *p*-nitroaniline
(c) *m*-nitroaniline (d) 2, 4, 6-trinitroaniline

28 Which of the following compounds will give significant amount of *meta-product* during mononitration reaction?
➞ JEE Main 2017

(a) 

(b) 

(c) 

(d) 

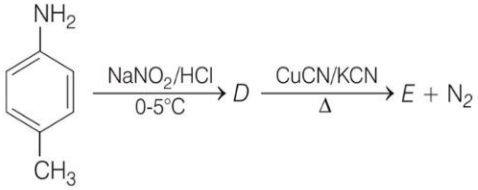
29 Benzene diazonium chloride reacts with hypophosphorous acid to produce

(a) benzene (b) phenol
(c) cyanobenzene (d) chlorobenzene

30 Fluorobenzene (C_6H_5F) can be synthesised in the laboratory

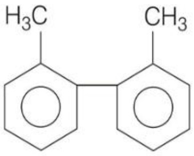
(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with HBF_4
(c) by direct fluorination of benzene with F_2 gas
(d) by reacting bromobenzene with NaF solution

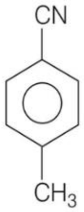
31 In the reaction,

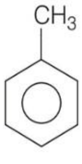


The product E is
➞ JEE Main 2015

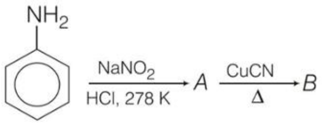
(a) 

(b) 

(c) 

(d) 

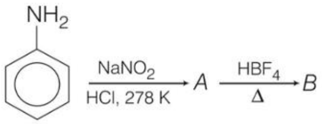
32 In the chemical reaction,



Compounds *A* and *B* respectively are

(a) fluorobenzene and phenol
(b) benzene diazonium chloride and benzonitrile
(c) nitrobenzene and chlorobenzene
(d) phenol and bromobenzene

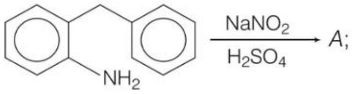
33 In the chemical reactions,



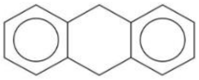
the compounds '*A*' and '*B*' respectively are ➞ AIEEE 2010

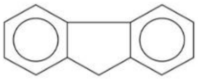
(a) nitrobenzene and fluorobenzene
(b) phenol and benzene
(c) benzene diazonium chloride and fluorobenzene
(d) nitrobenzene and chlorobenzene

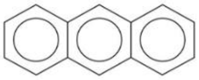
34

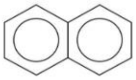


Product of this reaction is

(a)


(b)


(c)


(d)


Direction (Q. Nos. 35-36) *In the following questions, Assertion* (A) *followed by a Reason* (R) *is given. Choose the correct answer out of the following choices.*

(a) Assertion and Reason both are correct statements and Reason is the correct explanation of the Assertion
(b) Assertion and Reason both are correct statements but Reason is not the correct explanation of the Assertion
(c) Assertion is correct incorrect and Reason is incorrect
(d) Both Assertion and Reason are incorrect

35 Assertion (A) Hofmann's bromamide reaction is given by primary amides.

Reason (R) Primary amines in Hofmann's bromamide reaction follows acidic hydrolysis.

36 Assertion (A) Acylation of amine gives a monosubstituted product whereas alkylation of amines gives polysubstituted product

Reason (R) Acyl group sterically hinders the approach of further acyl groups

Direction (Q. Nos. 37-40) *Each of these questions contains two statements :* Statement I (Assertion) *and* Statement II (Reason). *Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below :*

(a) Statement I is true, Statement II is true; Statement II is a correct explanation for Statement I
(b) Statement I is true, Statement II is true; Statement II is not a correct explanation for Statement I
(c) Statement I is true; Statement II is false
(d) Statement I is false; Statement II is true

37 Statement I Amines are pyramidal in shape.

Statement II N-atom is sp^3-hybridised.

38 Statement I Aromatic amines are generally less basic than alkyl amines.

Statement II π-electrons in the ring decreases basic character.

39 Statement I In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

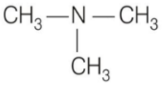
Statement II The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

40 Statement I Aniline on reaction with NaNO$_2$/HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate.

Statement II The colour of the compound formed in the reaction of aniline with NaNO$_2$/HCl at 0°C followed by coupling with β-naphthol is due to the extended conjugation.

PROGRESSIVE QUESTIONS EXERCISE

1 Compound '*A*' (C_3H_9N) reacts with benzene sulphonyl chloride to form a solid insoluble in alkali. The structure of compound '*A*' is

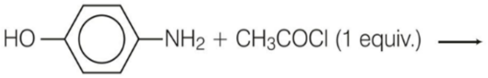
(a) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$

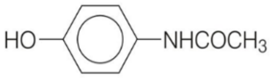
(b) $CH_3-CH_2-NH-CH_3$

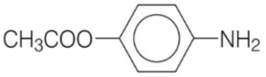
(c) $CH_3-CH_2-CH_2-NH_2$

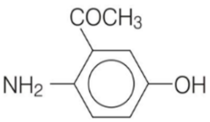
(d) All of these

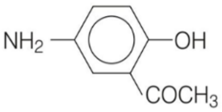
2 The main product formed in the reaction is



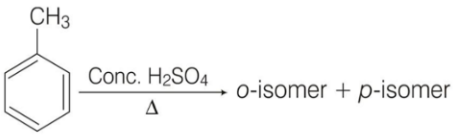
(a) 

(b) 

(c) 

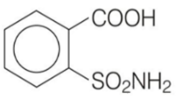
(d) 

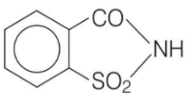
3 Consider the following reaction sequence

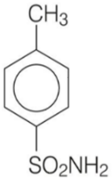


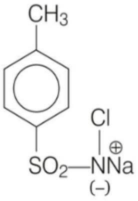
$$o\text{-isomer} \xrightarrow{PCl_5} \xrightarrow{NH_3} \xrightarrow[35°C]{aq.\ KMnO_4} \xrightarrow{\Delta} A$$

The structure of compound '*A*' is

(a) 

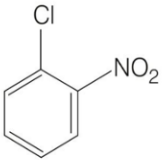
(b) 

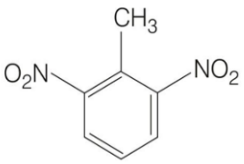
(c) 

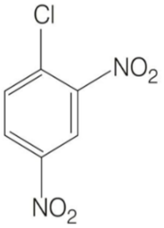
(d) 

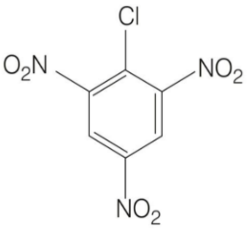
4 A major component of Borsch reagent is obtained by reacting hydrazine hydrate with which of the following?

→ JEE Main (Online) 2013

(a) 

(b) 

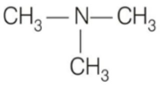
(c) 

(d) 

5 An organic compound containing C, H and N only was found to contain C = 61.03, N = 23.71. Its vapour density is 29.5. On treatment with nitrous acid, it gave nitrogen. The compound is

(a) $CH_3-CH(NH_2)-CH_3$

(b) $CH_3-CH_2-NH-CH_3$

(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$

(d) $CH_3-HC=CH-NH_2$

6 Reactants of reaction I are CH_3CONH_2, KOH, Br_2

Reactants of reaction II are CH_3NH_2, $CHCl_3$, KOH

The intermediate species of reaction I and reaction II are respectively

(a) carbonium ion, carbene

(b) carbene, nitrene

(c) nitrene, carbene

(d) carbocation, nitrene

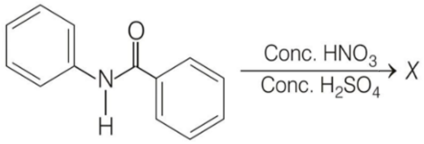
7 Which of the following reactions belong to electrophilic aromatic substitution?

(a) Bromination of acetanilide

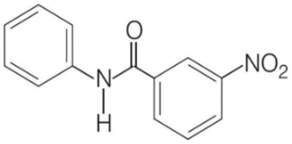
(b) Coupling reaction of aryldiazonium salts

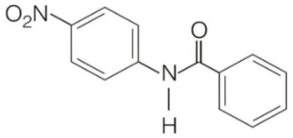
(c) Diazotisation of aniline

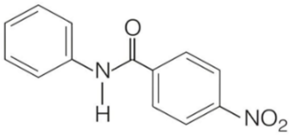
(d) Both (a) and (b)

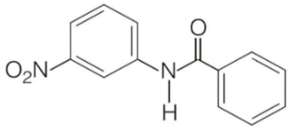
8 

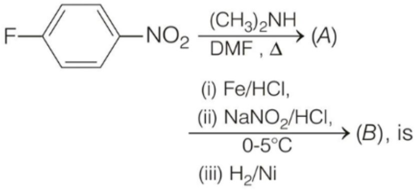
The structure of the major product X is

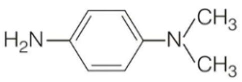
(a) 

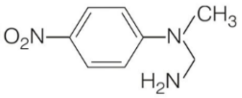
(b) 

(c) 

(d) 

9 

(a) 

(b) 

(c) 

(d) 

10. The best method to synthesise *m*-dibromobenzene is by using the reaction

(a) Benzene $\xrightarrow{Br_2/FeBr_3/heat}$

(b) Aniline $\xrightarrow{Br_2, H_2O}$ [ ] $\xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

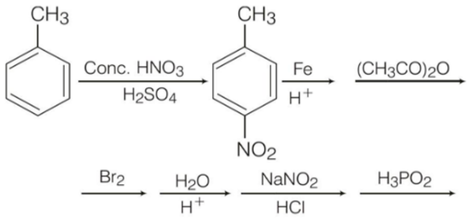
(c) Nitrobenzene $\xrightarrow[H_2SO_4,\,\Delta]{\text{Fuming } HNO_3}$ [ ] $\xrightarrow[C_2H_5OH,\text{ heat}]{Fe/HCl}$ [ ] $\xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

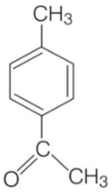
(d) Bromobenzene $\xrightarrow[H_2SO_4]{HNO_3}$ [ ] $\xrightarrow[C_2H_5OH,\text{ heat}]{Fe/HCl}$ [ ] $\xrightarrow[\text{(ii) CuBr}]{\text{(i) HONO}}$

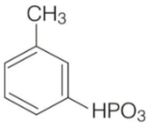
13 Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide solution. The reaction mixture so obtained contains

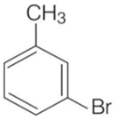
(a) mixture of *o*-and *p*-bromotoluenes
(b) mixture of *o*-and *p*-dibromobenzenes
(c) mixture of *o*-and *p*-bromoanilines
(d) mixture of *o*-and *m*-bromotoluenes

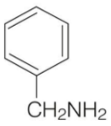
12 Consider the following reaction sequence
The final product of this reaction sequence is



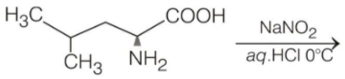
(a) 

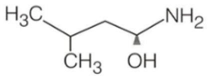
(b) 

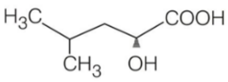
(c) 

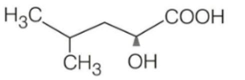
(d) 

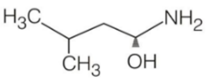
13 The major product of the reaction is



(a) 

(b) 

(c) 

(d) 

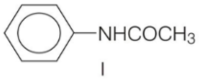
14 A compound (*X*) has the molecular formula C_7H_7NO. On treatment with Br_2 and KOH. (*X*) gives an amine (*Y*); (*Y*) gives carbylamine test. *(Y)* upon diazotisation and coupling with phenol gives an azodye (*Z*). (*X*) is

(a) $PhCONH_2$
(b) $PhCONHCOCH_3$
(c) $PhNO_2$
(d) $PhCOONH_4$

15 *(A)* is subjected to reduction with Zn-Hg/HCl and the product formed is N-methylmethanamine *(A)* can be

(a) ethane nitrile
(b) Nitroethane
(c) carbylamino ethane
(d) carbylamino methane

16 The correct order of basic strength of the following are



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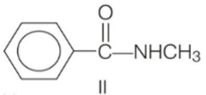

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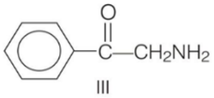
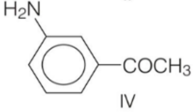


III



IV

(a) I > II > III > IV
(b) IV > II > III > I
(c) III > IV > II > I
(d) III > II > IV > I

ANSWERS

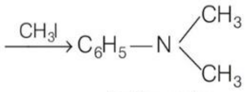
SESSION 1	1 (c)	2 (a)	3 (a)	4 (d)	5 (b)	6 (c)	7 (b)	8 (d)	9 (b)	10 (c)
	11 (c)	12 (c)	13 (d)	14 (a)	15 (c)	16 (b)	17 (d)	18 (b)	19 (d)	20 (a)
	21 (b)	22 (b)	23 (b)	24 (c)	25 (c)	26 (c)	27 (b)	28 (c)	29 (a)	30 (b)
	31 (c)	32 (b)	33 (c)	34 (b)	35 (c)	36 (c)	37 (b)	38 (c)	39 (d)	40 (a)
SESSION 2	1 (b)	2 (a)	3 (b)	4 (c)	5 (a)	6 (c)	7 (d)	8 (b)	9 (a)	10 (c)
	11 (a)	12 (c)	13 (d)	14 (a)	15 (c)	16 (d)				

Hints and Explanations

SESSION 1

1 $C_6H_5—NO_2 \xrightarrow[\text{Reduction}]{\text{Fe/HCl}} \underset{\text{Aromatic primary (1°) amine}}{C_6H_5—NH_2}$

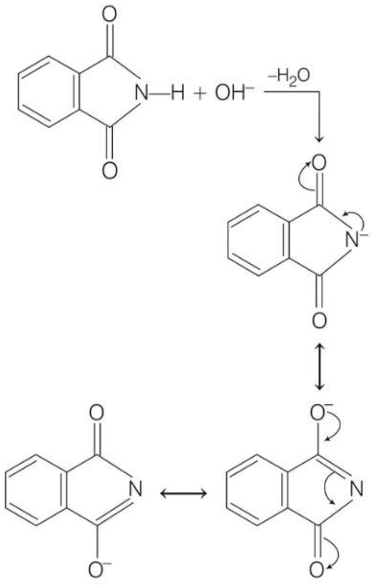
2 $C_6H_5NH_2 \xrightarrow{CH_3I} \underset{\text{Secondary amine}}{C_6H_5NHCH_3}$



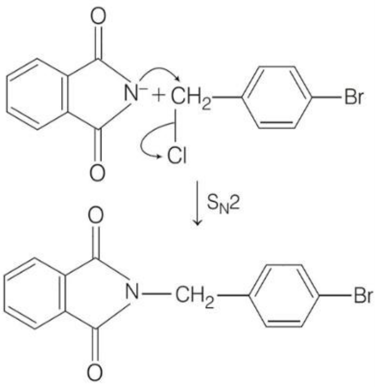
$\xrightarrow{CH_3I} C_6H_5—N(CH_3)_2$

Tertiary amine

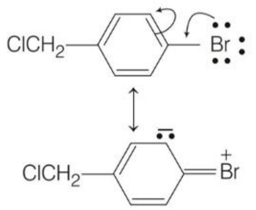
3 It is the first step of Gabriel's phthalimide synthesis, the hydrogen bonded to nitrogen is sufficiently acidic due to two α-carbonyls.



The conjugate base formed above act as nucleophile in the subsequent step of reaction. Nitrogen act as donor as it is better donor than oxygen.



Bromine is not substituted in the above reaction as it is in resonance with benzene ring giving partial double bond character to C—Br bond, hence difficult to break.



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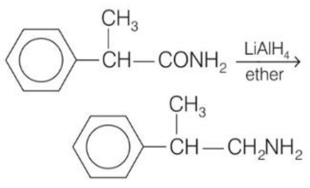


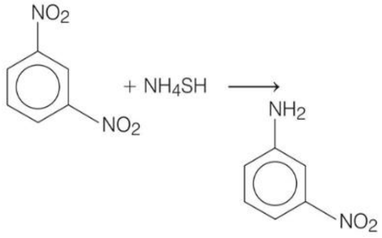
5 $\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{NaOH + Br_2} \underset{\text{Methylamine}}{CH_3NH_2}$

6 Hofmann-bromamide degradation reaction is given as:

$$RCONH_2 + 4NaOH + Br_2 \longrightarrow RNH_2 + NaCO_3 + 2NaBr + 2H_2O$$

Hence, four moles of NaOH and one mole of Br_2 are used.

7



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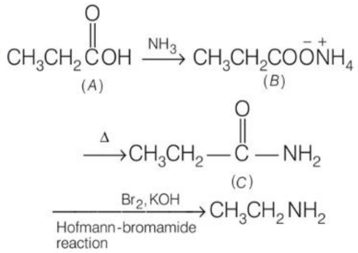


$$\underset{(A)}{CH_3CH_2\overset{O}{\overset{\|}{C}}OH} \xrightarrow{NH_3} \underset{(B)}{CH_3CH_2CO\overset{-}{O}\overset{+}{N}H_4} \xrightarrow{\Delta} \underset{(C)}{CH_3CH_2—\overset{O}{\overset{\|}{C}}—NH_2} \xrightarrow[\text{Hofmann-bromamide reaction}]{Br_2, KOH} CH_3CH_2NH_2$$

9 1° and 2° amines due to intermolecular H-bonding have higher boiling points (and hence less volatile) than 3° amines and hydrocarbons of comparable molecular mass. Further, due to polar C—N bonds, 3° amines are more polar than hydrocarbons which are almost non-polar. Therefore, due to weak dipole-dipole interactions, 3° amines have higher boiling point (i.e. less volatile) than hydrocarbons. In other words, $CH_3CH_2CH_3$ has the least boiling point and hence, is most volatile.

10 $(CH_3)_2$ NH acts as strong base, due to presence of two methyl groups with +*I*-effect, which intensifies negative charge on N-atom.

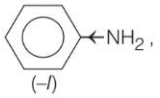
11 Dimethyl amine is the strongest base in aqueous solution due to solvation and inductive effect.

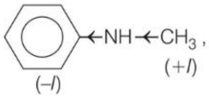
12 In gaseous state, as the number of alkyl group increases, electron density also increases and hence, the availability of electrons for donation increases, thus, basicity increases.

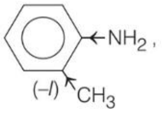
Hence, the correct order of basicity of amines in gaseous state is

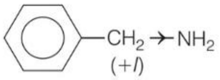
$3° > 2° > 1° > NH_3$.

13 $—CH_3$ (+*I*-effect) increases electron density at N-atom, hence basic nature is increased. C_6H_5 decreases electron density at N-atom, thus basic nature is decreased.

(a) 

(b) 

(c) 

(d) 

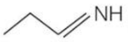
Thus, benzylamine (d) is the strongest base.

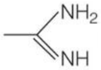
14 Order of basic strength of aliphatic amine in aqueous solution is as follows (order of K_b)

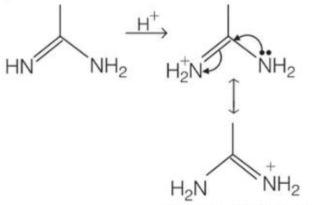
$(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N} > C_6H_5\ddot{N}H_2$

As we know, $pK_b = -\log K_b$. So, $(CH_3)_2\ddot{N}H$ will have smallest pK_b value. In case of phenyl amine, N is attached to sp^2-hybridised carbon, hence it has highest pK_b and least basic strength.

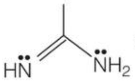
15 Among the given compounds the basic nature depends upon their tendency to donate electron pair.

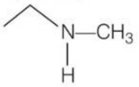
Since  is sp^2-hybridised. This marginally increases the electron negativity of nitrogen which in turn decreases the electron donating tendency of nitrogen. Thus making compound least basic.

Among the rest,  is totally different from others as in this compound lone pair of one nitrogen are in conjugation with π-bond i.e. as a result of this conjugation the cation formed after protonation become resonance stabilised.

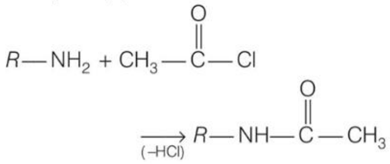


Equivalent resonance

This equivalent resonance in cation makes  most basic among all.

Categorisation is very simple between rest two as  (primary amine) is less basic than  (secondary amine).

Hence, the correct order is II < I < IV < III, i.e. option (c) is correct.

16 

$$R-NH_2 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow[(-HCl)]{} R-NH-\overset{O}{\overset{\|}{C}}-CH_3$$

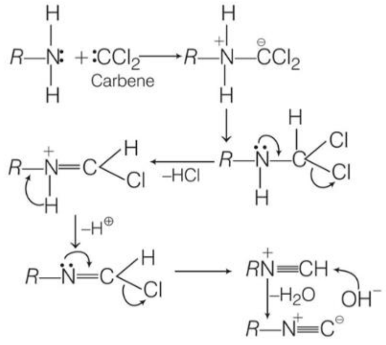
Since, each $—COCH_3$ group displace one H atom in the reaction of one mole of $CH_3—\overset{O}{\overset{\|}{C}}—Cl$ with one $—NH_2$ group, the molecular mass increases with 42 unit. Since, the mass increases by (390 – 180) = 210 hence the number of $—NH_2$ group is $\frac{210}{42} = 5$.

17 This reaction is an example of carbylamine reaction which includes conversion of amine to isocyanide.

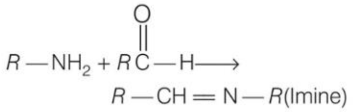
$$\underset{1°\text{amine}}{R-\ddot{N}H_2} + CHCl_3 \xrightarrow[KOH]{C_2H_5OH} \underset{\text{Alkyl isocyanide}}{R-\overset{+}{N}\equiv\overset{-}{C}:}$$

18 The mechanism of carbylamine reaction is given below :

$$CHCl_3 \xrightarrow[\alpha\text{-elimination}]{OH^-} \underset{\text{Dichlorocarbene}}{:CCl_2}$$



19 When amines reacts with an aldehyde then imines are formed.



$$R-NH_2 + R\overset{O}{\overset{\|}{C}}-H \longrightarrow R-CH=N-R\text{(Imine)}$$

20 $(C_2H_5)_2NH + HNO_2 \xrightarrow[-H_2O]{} \underset{\text{Nitrosoamine}}{(C_2H_5)_2N\cdot N{=}O}$

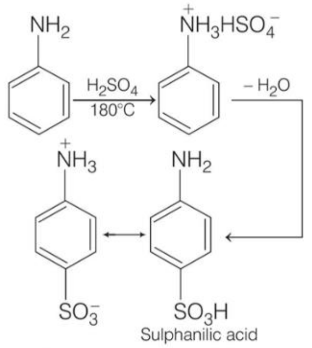
21 $C_6H_5SO_2Cl + RNH_2 \longrightarrow \underset{\substack{\text{N- alkyl benzene}\\\text{sulphonamide}\\\text{(Soluble in KOH)}}}{RNHSO_2C_6H_5} + HCl$

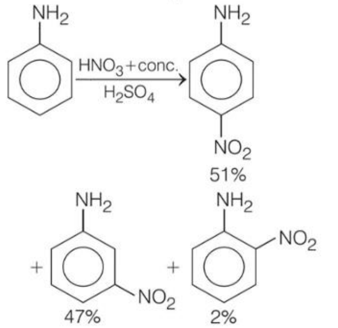
$\xrightarrow{KOH} [R-\bar{N}SO_2C_6H_5]K^+ + H_2O$

22 Wurtz reaction is used to prepare alkanes from alkyl halides.

$$2R-X + 2Na \xrightarrow{\text{Dry ether}} R-R + 2NaX$$

23 A ⟶ 4; B ⟶ 3; C ⟶ 1; D ⟶ 2

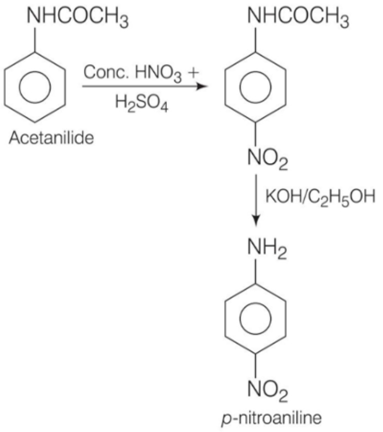
24. 

25. 

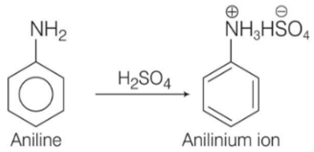
Nitration of aniline also gives *m*-nitroaniline in strong acidic medium because in strong acidic conditions, protonation of —NH_2 group gives anilinium ion (NH_3^+) which is deactivating and *m*-directive in nature.

26 The disubstituted benzene in which all the four hydrogen atoms are identical, will give only one monosubstituted product. i.e. *p*-dinitrobenzene.

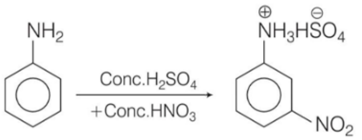
27 *p*-nitroaniline is obtained as a major product by the nitration of acetanilide followed by alkaline hydrolysis.



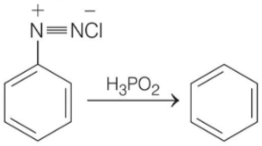
28 Aniline in presence of nitrating mixture (conc. HNO_3 + conc. H_2SO_4) gives significant amount(≈ 47%) of *meta*-product because in presence of H_2SO_4 its protonation takes place and anilinium ion is formed.



Here, anilinium ion is strongly deactivating group and *meta*-directing in nature. So, it gives *meta*-nitration product.



29 Benzene diazonium chloride undergoes deamination upon reaction with hypophosphorus acid and gives benzene.



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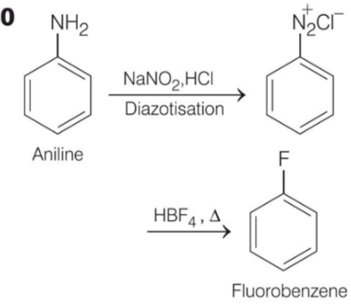

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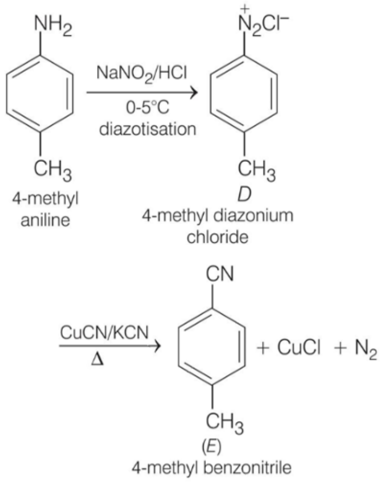
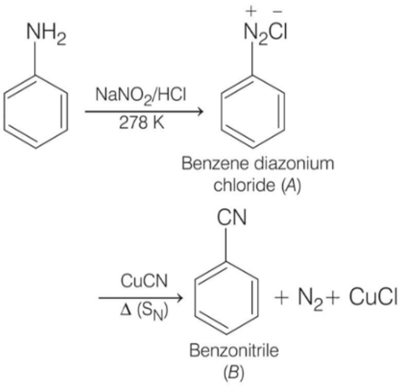


32 Formation of (*A*) is by diazotisation and formation of *B* from *A* is by S_N reaction.



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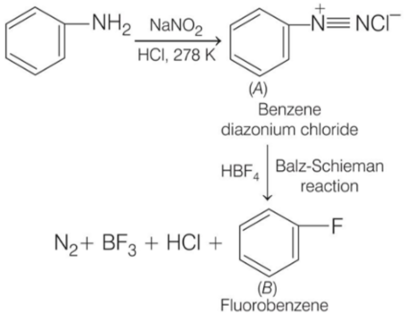

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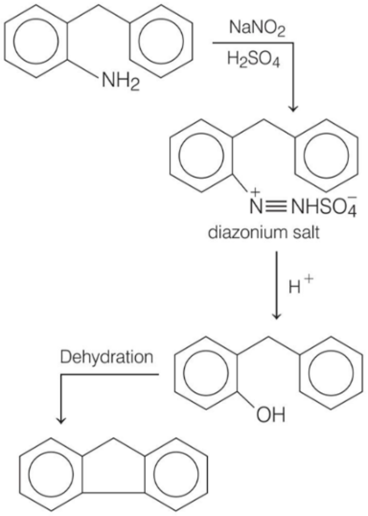


35 **Correct Reason** With Br_2 / NaOH, primary amides are converted into isocyanates which upon alkaline hydrolysis give primary amines.

36 **Correct Reason** Due to delocalisation of the lone pair of electrons of the N-atom over the carbonyl group in the acyl derivative, the electron density on the N-atom decreases to such an extent that it does not act as a nucleophile at all and hence, does not react with another molecule of the acylating agent.

37 It is true that nitrogen atom in amine is sp^3-hybridised but due to the presence of lone pair of electrons, the angle C—N—*E* (where, *E* is C or H) is less than 109.5°. It is 108° in case of trimethyl amine (pyramidal shape).

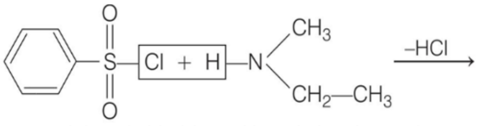
38 Aromatic amines are less basic than alkyl amines and ammonia due to the electron withdrawing nature of the aryl group. π-electrons are responsible for resonance effect.

39 In strongly acidic medium, aniline gets protonated, so lone pair of electrons are not available to produce mesomeric or electromeric effects. Thus, aniline becomes less reactive.

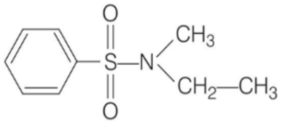
40 Aniline on reaction with $NaNO_2$ + HCl at 0°C followed by coupling with β-naphthol gives a dark blue coloured precipitate is due to the extended conjugation.

SESSION 2

1

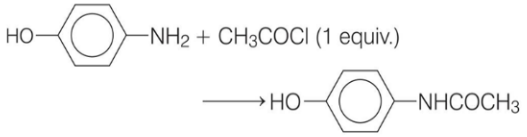


Benzenesulphonyl chloride N-methylmethanamine (2° amine)



N-ethyl, N-methylbenzene sulphonamide (insoluble in alkali)

2 $—NH_2$ is more activated than —OH. Hence, $—NH_2$ is attacked by CH_3COCl.



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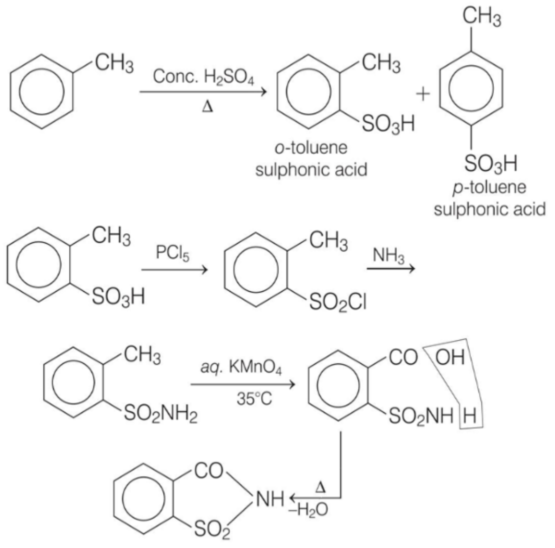
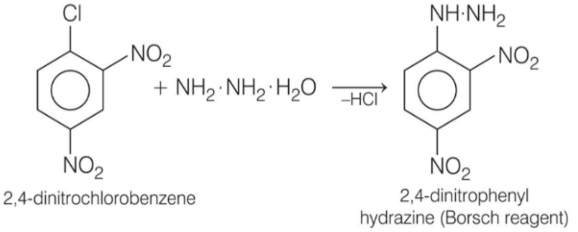


4 Borsch reagent is 2,4-dinitrophenyl hydrazine, thus, it is obtained by treating 2,4-dinitrochlorobenzene with hydrazine hydrate.



5. (i) For empirical formula

Element	%	Molar ratio	Simplest ratio
C	61.03	$\frac{61.03}{12} = 5.08$	$\frac{5.08}{1.69} = 3$
H	15.26	$\frac{15.26}{1} = 15.26$	$\frac{15.26}{1.69} = 9$
N	23.71	$\frac{23.71}{14} = 1.69$	$\frac{1.69}{1.69} = 1$

∴ Empirical formula is C_3H_9N and empirical formula weight = 59

Given, molecular weight = Vapour density × 2 = 29.5 × 2 = 59

$$\therefore \qquad n = \frac{59}{59} = 1$$

∴ Molecular formula is C_3H_9N.

(ii) The amine loses N_2 on treatment with HNO_2 and thus, it is a primary amine. Thus, compound is

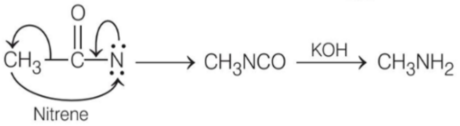
$CH_3—CH_2—CH_2—NH_2$ or $CH_3—CH(NH_2)—CH_3$

Propanamine Propan-2-amine

$$(CH_3)_2CHNH_2 + HNO_2 \longrightarrow N_2 + (CH_3)_2CHOH + H_2O$$

6 Reaction I

$$CH_3CONH_2 \xrightarrow{Br_2} CH_3CONHBr \xrightarrow[-\,KBr]{KOH}$$



Reaction II

$$CHCl_3 + KOH \longrightarrow H_2O + \underbrace{:CCl_3 + K^+}$$

$$\downarrow$$

$$KCl + :CCl_2$$

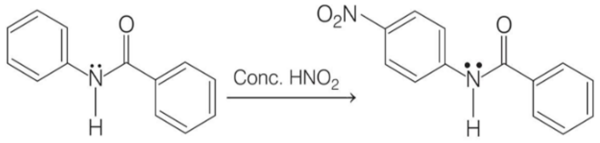
(Carbene)

$$:CCl_2 \xrightarrow{CH_3NH_2} CH_3NC$$

Dichloro carbene

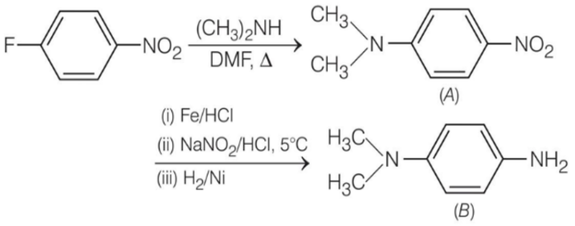
7 Bromination of acetanilide and coupling reactions of diazonium salts both are the examples of electrophilic substitution reaction.

8



Since, ring 1 is more active, electrophilic substitution takes place over ring 1. Further more $—NH—\underset{\underset{O}{\|}}{C}—Ph$ is *ortho-para* directing in nature and *para* product is predominating.

9



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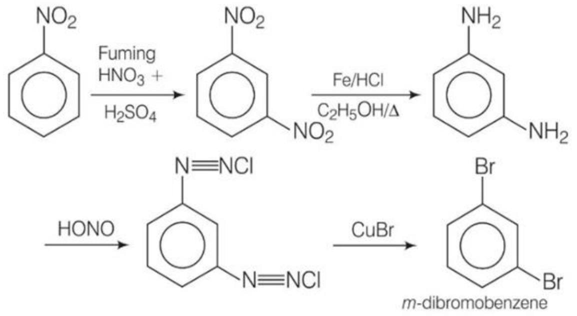

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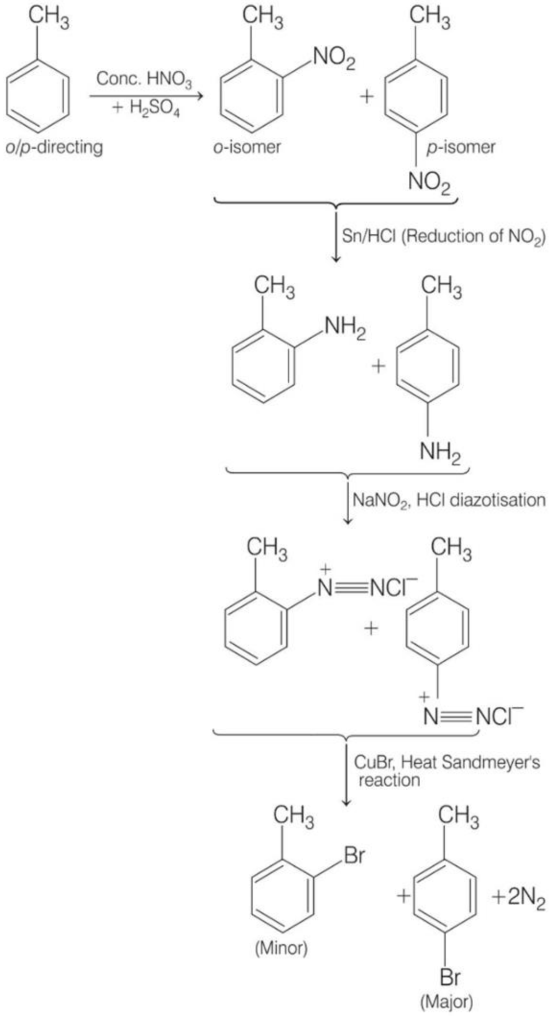
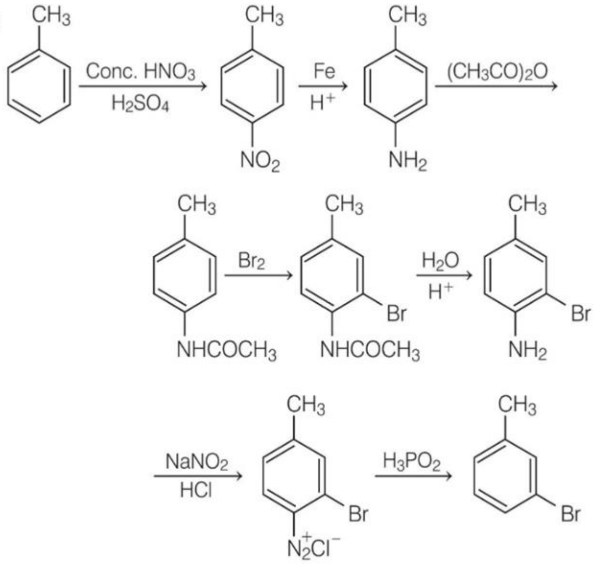


o- and p-bromotoluenes

12



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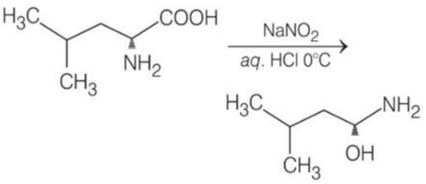

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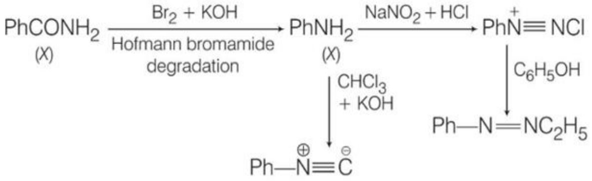


15 CH_3NC (carbylamino methane) when subjected to reduction with Zn-Hg/HCl forms N-methyl methanamine

$$CH_3-NC \xrightarrow[\text{HCl}]{\text{Zn-Hg/}} CH_3NHCH_3$$

16 Electron releasing groups increase the basic strength of amines whereas, electron withdrawing groups decrease it. Therefore, III > II > I > IV, since in $NHCOCH_3$, —NH group is placed between two electron withdrawing groups.

PRACTICE SET - 02

A SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

1. Nitrobenzene can be reduced to aniline by

$\underset{I}{H_2/Ni}$ $\underset{II}{Sn/HCl}$

$\underset{III}{Zn/NaOH}$ $\underset{IV}{LiAlH_4}$

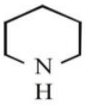
(a) I, II and III (b) I and II
(c) I, II and IV (d) only II

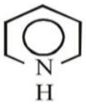
2. 

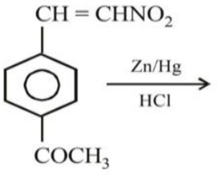
Z; Z is

(a) 

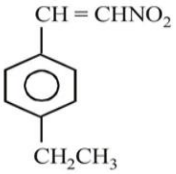
(b) 

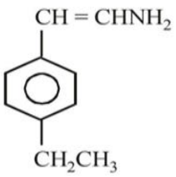
(c) 

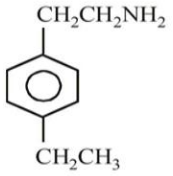
(d) 

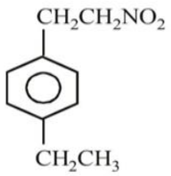
3. 

Product. Here the product is

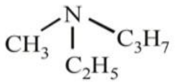
(a) 

(b) 

(c) 

(d) 

4. Which statement is true regarding the following structure?



(a) It is a chiral molecule
(b) It exists in two resolvable optically active forms
(c) Both a) and b) (d) Neither a) nor b)

5. Introduction of a methyl group in ammonia markedly increases the basic strength of ammonia in aq. solution, introduction of the second methyl group increases only marginally the basic strength of methyl amine in water. This is due to

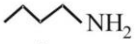
(a) different type of hybridisation in the two amines
(b) protonated dimethyl amine is more solvated than methyl amine
(c) protonated dimethyl amine is more solvated than the protonated methyl amine
(d) protonated dimethyl amine is less stable than the protonated methyl amine

6. The basic character of ethyl amine, diethyl amine and triethyl amine in chlorobenzene is

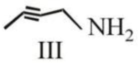
(a) $C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$
(b) $C_2H_5NH_2 < (C_2H_5)_3N < (C_2H_5)_2\,NH$
(c) $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2$
(d) $(C_2H_5)_3N < C_2H_5NH_2 < (C_2H_5)_2NH$

MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ				

7. The correct order of decreasing basic character of the three aliphatic primary amines is

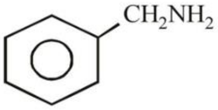

I

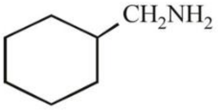

II


III

(a) I > II > III (b) III > II > I
(c) I > II ≈ III (d) I = II ≡ III

8. Which of the statement is true regarding the basicity of the following two primary amines ?


I


II

(a) Both are equally basic because both are 1° amines
(b) I > II because it is an aromatic amine
(c) II > I because it is an aliphatic amine
(d) I < II because of difference in the nature of β-carbon

9. The correct order of decreasing basic character is

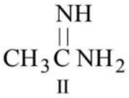
$\underset{I}{C_6H_5NH_2}$, $\underset{II}{C_6H_5CH_2NH_2}$,

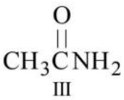
$\underset{III}{(C_6H_5)_2NH}$, $\underset{IV}{C_6H_{11}NH_2}$

(a) II > I > III > IV (b) IV > II > I > III
(c) IV > III > II > I (d) IV > II > III > I

10. The correct order of increasing basicity is

$\underset{I}{CH_3CH_2NH_2}$

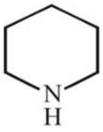

$\underset{II}{CH_3\overset{\overset{NH}{||}}{C}NH_2}$


$\underset{III}{CH_3\overset{\overset{O}{||}}{C}NH_2}$

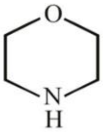
(a) II < III < I (b) I ≈ III < II
(c) I < II < III (d) III < I < II

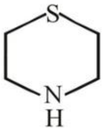
11. The relative order of basic character of the following compounds is


I


II


III


IV


V

(a) II > I > III > IV > V (b) II > III > IV > V > I
(c) II > V > IV > I > III (d) II > IV > V > III > I

12. When aniline is treated with acetyl chloride in presence of anhydrous aluminium chloride, the main product is

(a) *o* - aminoacetophenone (b) *p*-aminoacetophenone
(c) both (a) and (b) (d) *m*-aminoacetophenone

13. $CH_3CH_2CH_2NH_2 \xrightarrow[0^\circ C]{NaNO_2,\ HCl} P$. P is

(a) $CH_3CH_2CH_2OH$ (b) $(CH_3)_2CHCl$
(c) Both (a) and (b) (d) Reaction not possible

14. Benzenediazonium chloride when treated with phenols gives azo dyes, to get best result the pH of the medium should be

(a) around 4 (b) around 8
(c) around 10 (d) 12

15. In the following reaction, the reagent X should be

$$RCOOH + [X] \xrightarrow{\text{conc. } H_2SO_4} RNH_2$$

(a) NH_3 (b) HN_3
(c) either of the two (d) None of the two

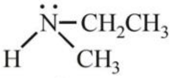
16. Which of the following can undergo electrophilic substitution when treated with nitrous acid at 0° C ?

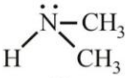
(a) $C_6H_5NH_2$ (b) $C_6H_5NHCH_3$
(c) $C_6H_5N(CH_3)_2$ (d) None

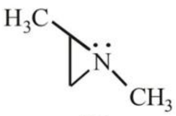
17. Which of the following does not reduce $C_6H_5NO_2$ to aniline ?

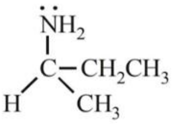
(a) Sn/HCl (b) $SnCl_2$/HCl
(c) Zn/HCl (d) $LiAlH_4$

18. Which of the following amines can be resolved into two enantiomers?


I


II


III


IV

(a) I, IV (b) I, II
(c) I, III, IV (d) III, IV

MARK YOUR RESPONSE	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ
	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ
	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ			

19. Which of the following statement is false?

(a) Dimethyl amine as well as trimethyl amine are soluble in water

(b) Trimethyl amine forms hydrogen bond neither with itself nor with water.

(c) Trimethyl amine can act as hydrogen bond acceptor only, while dimethyl amine can serve as both a hydrogen bond donor and acceptor

(d) All the three statements are false

20. Ephedrine is a secondary amine. It is widely used in cold and allergy conditions in the form of its hydrochloride but not as such because

(a) the amine itself has unpleasant smell, while its salt is odourless

(b) the amine is insoluble in water, while the salt is soluble in water

(c) the amine is unstable and easily oxidised by air, while the salt is resistant to atmospheric oxidation

(d) of all the above facts

21. Benzamide and benzyl amine can be distinguished by

(a) cold dil. NaOH

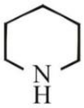
(b) cold dil. HCl

(c) both a & b

(d) $NaNO_2$, HCl, 0°C, then β-naphthol

22. The correct order for the basic character of the compounds I to IV should be

I



II

III

CH_3CN

IV

(a) IV < III < I < II (b) IV < I < III < II
(c) IV < II < III < I (d) IV < III<II< I

23. Which of the following is true regarding basic character of pyridine and pyrrole?

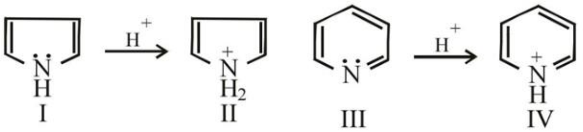
(a) Pyrrole is more basic because its nonbonding electrons occupy sp^3 orbital

(b) Pyridine is more basic because its nonbonding electrons is not a part of aromatic sextet.

(c) Both are equally basic

(d) Pyridine is less basic because it is 3° amine

24. Pyrrole and pyridine both are basic and form salts with acids?



Which of the following statement is true regarding the aromatic character of the four species?

(a) All the four are aromatic

(b) I, III and IV are aromatic

(c) I, II and III are aromatic

(d) I and III are aromatic

25. Ethylene can be prepared in good yield by

(a) $$CH_3CH_2N^+(CH_3)_3I^- \xrightarrow{heat} CH_2 = CH_2 + (CH_3)_3N + HI$$

(b) $$CH_3CH_2N^+(CH_3)_3OH^- \xrightarrow{heat} CH_2 = CH_2 + (CH_3)_3N + H_2O$$

(c) Both a and b

(d) $CH_3CH_2NH_2 \xrightarrow{heat} CH_2 = CH_2 + NH_3$

26. Which one of the following is not an oxidation product of a primary amine?

(a) A hydroxylamine (b) A nitroso compound
(c) A nitro compound (d) None of these

27. Which of the following method is used for eliminating nitrogen of an amine present outside the ring?

(a) Hofmann elimination (b) Cope elimination
(c) Both (d) Emde degradation

28. Which of the following does not react with nitrous acid?

(a) $C_6H_5NH_2$ (b) $C_6H_5NHCH_3$
(c) $C_6H_5N(CH_3)_2$ (d) None of these

29. Which of the following leads to carbon-carbon double bond?

(a) 1° Amine + RCHO → (b) 2° Amine + R_2CO →
(c) 2° Amine + RCHO → (d) both b & c

30. Electrophilic aromatic substitution of pyridine resembles with

(a) benzene (b) aniline
(c) nitrobenzene (d) none of these

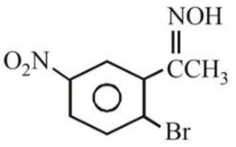
MARK YOUR RESPONSE	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ
	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ
	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ			

31. Which of the following will react most readily with NaOH to form ethanol ?

(a) $(CH_3)_4N^+I^-$ (b) $(CH_3)_4S^+I^-$

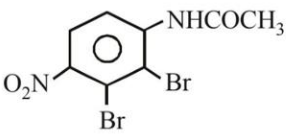
(c) $(CH_3)_3CCl$ (d) CH_3OCH_3

32.

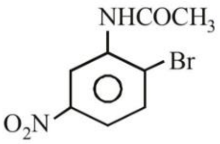


$\xrightarrow[\text{Heat}]{\text{Conc. } H_2SO_4}$ Product is

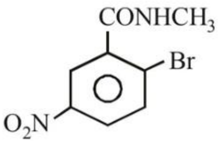
(a)



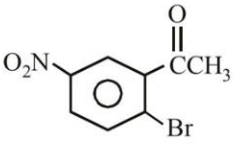
(b)



(c)



(d)



33. In Hofmann bromamide degradation, one of the important steps is the migration of

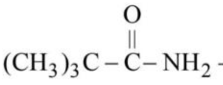
(a) an alkyl group without its electron pair to electron deficient N atom

(b) an alkyl group with its electron pair to electron deficient O atom

(c) an alkyl group with its electron pair to electron rich N atom

(d) an alkyl group with its electron pair to electron deficient N atom

34.



$(CH_3)_3C-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[\text{(ii)}D_2O]{\text{(i) }OD^-/Br_2}$ Product P is

(a) $(CH_3)_3CNH_2$ (b) $(CH_3)_3CNHD$

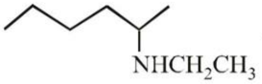
(c) $(CH_3)_3CND_2$ (d) no reaction

35. Reaction of ethyl amine with alkaline **chloroform** leads to the formation of carbylamine reaction. This reaction involves the attack of an electrophile on ethyl amine, the electrophile is

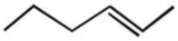
(a) H_3O^+ (b) H^+

(c) RNH^+_3 (d) $:CCl_2$

36. Predict the possible number of alkenes and the main alkene in the following reaction.



$\xrightarrow[\text{(ii) }Ag_2O]{\text{(i) excess }CH_3I}$ [ ] $\xrightarrow{\text{heat}}$ Product

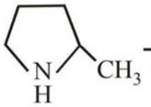
(a) 2 and 

(b) 2 and 

(c) 3 and $H_2C=CH_2$

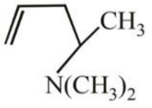
(d) 2 and $H_2C=CH_2$

37.

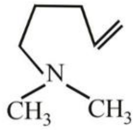


$\xrightarrow[\text{(ii) }Ag_2O\text{, heat}]{\text{(i) }CH_3I}$ Product P is

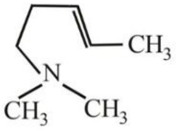
(a)



(b)

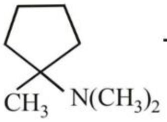


(c)



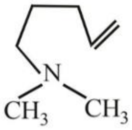
(d) None

38.



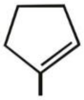
$\xrightarrow[\text{(ii) heat}]{\text{(i) }H_2O_2}$ Product P is

(a)

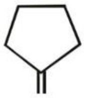


(b)

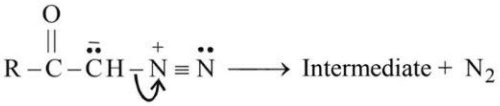
(c)



(d)



MARK YOUR RESPONSE					
	31. ⓐⓑⓒⓓ	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ
	36. ⓐⓑⓒⓓ	37. ⓐⓑⓒⓓ	38. ⓐⓑⓒⓓ		

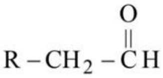
39. 
$R-\overset{O}{\overset{\|}{C}}-\overset{\cdot\cdot}{\overset{-}{C}}H-\overset{+}{N}\equiv\overset{\cdot\cdot}{N} \longrightarrow \text{Intermediate} + N_2$

What is the nature of its intermediate in this reaction ?

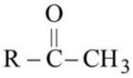
(a) Carbonium ion (b) Carbanion

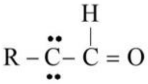
(c) Carbene (d) Free radial

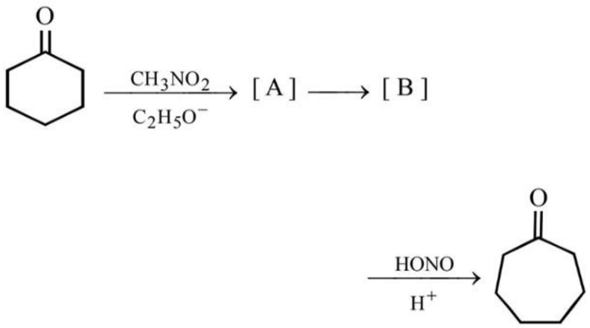
40. The intermediate formed in the above reaction rearranges to

(a) 
$R-CH_2-\overset{O}{\overset{\|}{C}}H$

(b) $R-CH=C=O$

(c) 
$R-\overset{O}{\overset{\|}{C}}-CH_3$

(d) 
$R-\underset{\cdot\cdot}{\overset{\cdot\cdot}{C}}-\overset{H}{\overset{|}{C}}=O$

41. 

Which reaction is/are involved in the above conversion?

(a) Diazotisation and Beckmann rearrangement

(b) Diazotisation and Robinson annulation

(c) Aldol condensation and diazotisation

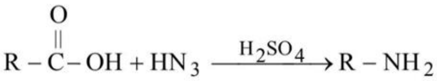
(d) Diazotisation and pinacol type of rearrangement

42. Which of the reaction can not be used for introducing a C = C linkage?

(a) Hofmann elimination (b) Aldol condensation

(c) Wittig reaction (d) None of the three

43. Following reaction is an example of


$R-\overset{O}{\overset{\|}{C}}-OH + HN_3 \xrightarrow{H_2SO_4} R-NH_2$

(a) Hofmann reaction (b) Curtius reaction

(c) Schmidt reaction (d) Lossen reaction

44. Which of the following is one of the intermediates in Hofmann, Curtius, Schmidt and Lossen reaction ?

(a) $R\overset{+}{C}O$ (b) RNCO

(c) RCNO (d) $RCO\overset{-}{N}H$

45. Which of the following involves migration to electron-deficient nitrogen?

(a) Benzilic acid rearrangement

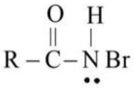
(b) Wolf rearrangement

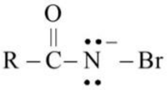
(c) Allylic rearrangement

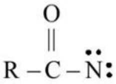
(d) Beckmann rearrangement

46. Which of the following is not formed as an intermediate in the Hofmann rearrangement?

$$R-CONH_2 \xrightarrow{Br_2/NaOH} RNH_2$$

(a) 
$R-\overset{O}{\overset{\|}{C}}-\underset{\cdot\cdot}{\overset{H}{\overset{|}{N}}}Br$

(b) 
$R-\overset{O}{\overset{\|}{C}}-\underset{\cdot\cdot}{\overset{\cdot\cdot -}{N}}-Br$

(c) 
$R-\overset{O}{\overset{\|}{C}}-\overset{\cdot\cdot}{N}:$

(d) All the three are formed

47. Identify (C) and (D) in the following series of reactions

$$CH_3NH_2 \xrightarrow[CH_3I]{\text{excess of}} [A] \xrightarrow{AgOH} [B] \xrightarrow{\text{heat}} [C]+[D]$$

(a) $(CH_3)_3COH$, CH_3NH_2

(b) $(CH_3)_2C = CH_2$, CH_3NH_2

(c) $(CH_3)_3N$, CH_3OH

(d) $(CH_3)_2C=CH_2$, CH_3OH

48. Identify (D) and (E) in the given reaction

$$CH_3COOH \xrightarrow[\text{(ii) } PBr_3]{\text{(i) } LiAlH_4} (A) \xrightarrow[\text{(ii) } LiAlH_4]{\text{(i) } KCN} (B)$$

$$\xrightarrow{CHCl_3/OH^-} (C) \xrightarrow{\text{hydrolysis}} (D)+(E)$$

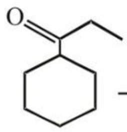
(a) $CH_3CH_2CH_2NHCH_3$

(b) $(CH_3)_2CHNH_2$, HCOOH

(c) $CH_3CH_2CH_2NH_2$, HCOOH

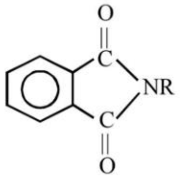
(d) $CH_3CH_2CH_2COOH$

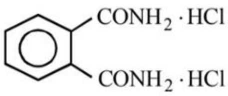
MARK YOUR RESPONSE	39. ⓐⓑⓒⓓ	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ
	44. ⓐⓑⓒⓓ	45. ⓐⓑⓒⓓ	46. ⓐⓑⓒⓓ	47. ⓐⓑⓒⓓ	48. ⓐⓑⓒⓓ

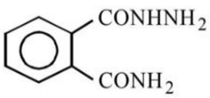
49.  $\xrightarrow{NH_2OH} [\ ] \xrightarrow[\text{heat}]{\text{conc. } H_2SO_4} [\ ] \xrightarrow{H^+} [Z]$;

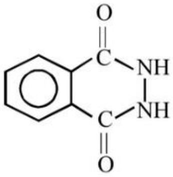
Z is

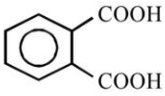
(a) a single compound
(b) a mixture of two compounds
(c) a mixture of three compounds
(d) a mixture of four compounds

50.  $\xrightarrow[\text{(ii) HCl}]{\text{(i) } NH_2NH_2.H_2O}$ Product is

(a) 

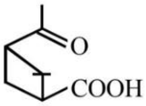
(b) 

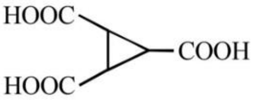
(c) 

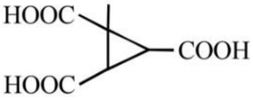
(d) 

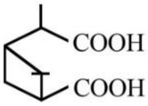
51.  $\xrightarrow[\text{(ii) Heat with Cu powder}]{\text{(i) } CHN_2COOC_2H_5} [Y] \xrightarrow{\text{oxidation}} [Z]$

Compound Z should be

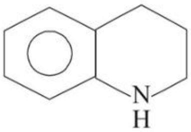
(a) 

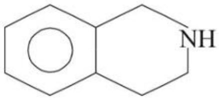
(b) 

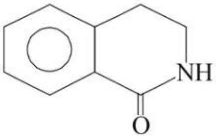
(c) 

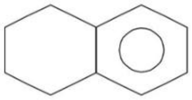
(d) 

52. Which of the following undergoes bromination most easily ?

(a) 

(b) 

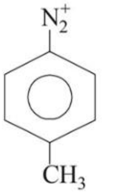
(c) 

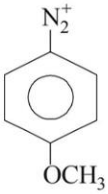
(d) 

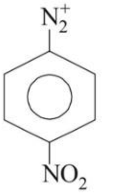
53. How many structural isomers of a Grignard reagent are possible for preparing *n*-butane by reaction with ethyl amine ?

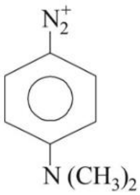
(a) 1 (b) 2
(c) 3 (d) 4

54. For the diazonium ions, the order of reactivity towards diazo-coupling with phenol in the presence of dil.NaOH is

I 

II 

III 

IV 

(a) I < IV < II < III (b) IV < II < I < III
(c) I < II < IV < III (d) III < IV < II < I

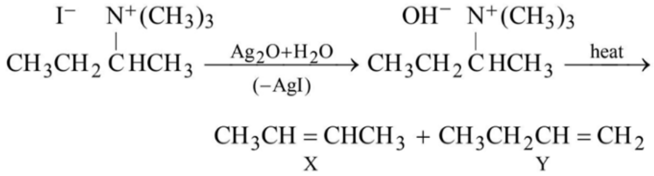
MARK YOUR RESPONSE	49. ⓐⓑⓒⓓ	50. ⓐⓑⓒⓓ	51. ⓐⓑⓒⓓ	52. ⓐⓑⓒⓓ	53. ⓐⓑⓒⓓ
	54. ⓐⓑⓒⓓ				

B COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

When a quaternary ammonium halide is treated with moist silver oxide (a slurry of Ag_2O in water), a quaternary ammonium hydroxide is formed as the main product. Thermal decomposition of the quaternary ammonium hydroxide gives an alkene. This reaction is known as Hofmann elimination and has most of the characteristics of an E2 reaction.



$$CH_3CH_2\overset{\overset{I^-\ \ N^+(CH_3)_3}{|}}{C}HCH_3 \xrightarrow[(-AgI)]{Ag_2O+H_2O} CH_3CH_2\overset{\overset{OH^-\ \ N^+(CH_3)_3}{|}}{C}HCH_3 \xrightarrow{heat} \underset{X}{CH_3CH=CHCH_3} + \underset{Y}{CH_3CH_2CH=CH_2}$$

1. The Hofmann eliminations are
(i) concreted (ii) *anti*-stereoselective
(iii) occur in separate steps (iv) *syn*-stereoselective
(a) (i) and (iv) (b) (i) and (ii)
(c) Only (i) (d) Only (iii)

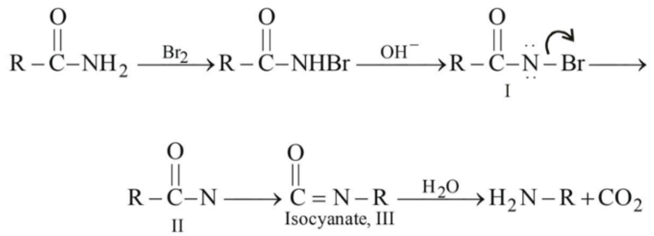
2. In the above reaction, which of the following is correct regarding yield of X and Y?
(a) $X = Y$ (b) $X \approx Y$
(c) $X > Y$ (d) $X < Y$

PASSAGE-2

The conversion of an amide to an amine with one carbon atom less by the action of alkaline hypohalite is known as Hofmann degradation.

$$RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2$$

The most important feature of the reaction is the rearrangement of N-bromamide anion to isocyanate :



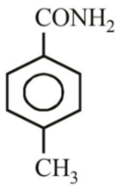
$$R-\overset{\overset{O}{||}}{C}-NH_2 \xrightarrow{Br_2} R-\overset{\overset{O}{||}}{C}-NHBr \xrightarrow{OH^-} \underset{I}{R-\overset{\overset{O}{||}}{C}-\underset{..}{\overset{..}{N}}-Br} \longrightarrow \underset{II}{R-\overset{\overset{O}{||}}{C}-N} \longrightarrow \underset{\text{Isocyanate, III}}{\overset{\overset{O}{||}}{C}=N-R} \xrightarrow{H_2O} H_2N-R+CO_2$$

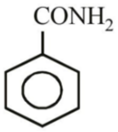
Hofmann reaction is accelerated if the migrating group is more electron-releasing.

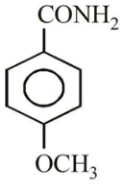
3. Which step is the driving force in the above reaction to proceed in right direction?
(a) conversion of I to II
(b) conversion of II to III
(c) conversion of III to RNH_2
(d) All

This passage has appeared in IIT/JEE 2006

4. Which of the following can undergo Hofmann reaction most easily?

(a)


(b)


(c)


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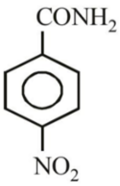

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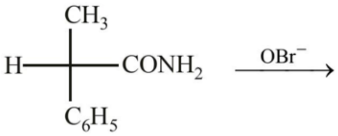


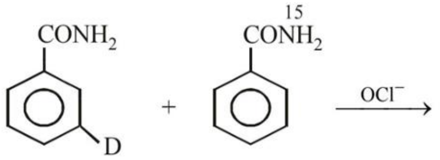
$$H-\underset{\underset{C_6H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-CONH_2 \xrightarrow{OBr^-}$$ Product amine will be

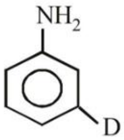
(+) – α-Phenylpropionamide

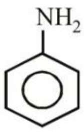
(a) (+) – (b) (–) –
(c) 50 : 50 racemic (d) non-50 : 50 racemic

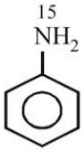
MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

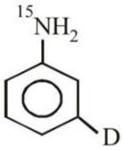
6. Predict the product in the following reaction :



(i)


(ii)


(iii)


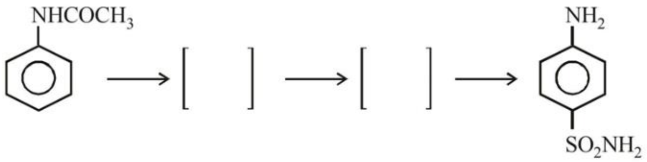
(iv)


(a) (i) and (ii)
(b) (ii) and (iii)
(c) (i) and (iii)
(d) All the four

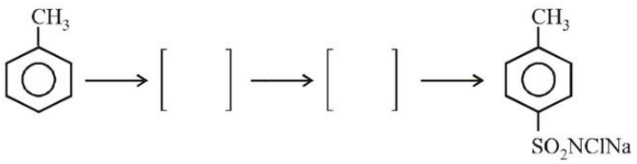
PASSAGE-3

Understand carefully the following two reactions and answer the questions mentioned below.

Reaction (i)



Reaction (ii)



7. Which of the steps is(are) common in the two reactions?

(a) 1st step
(b) 2nd step
(c) both
(d) none

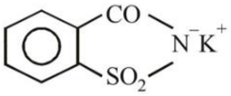
8. Which of the final products are medicinally important?

(a) Product from reaction (i)
(b) Product from reaction (ii)
(c) Products from both reactions
(d) None of the two products

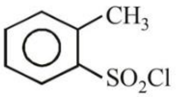
9. Which one of the following reagent can be used for the introduction of Cl and Na in reaction (ii)?

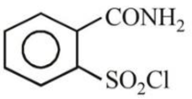
(a) Cl_2 / Na_2CO_3
(b) HCl / NaOH
(c) NaCl / NaOH
(d) NaOCl / NaOH

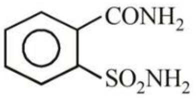
10. Saccharin, an important sweetening agent, of the following structure

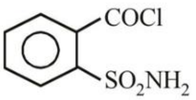


is prepared by one of the products of the reaction (ii), that product should be

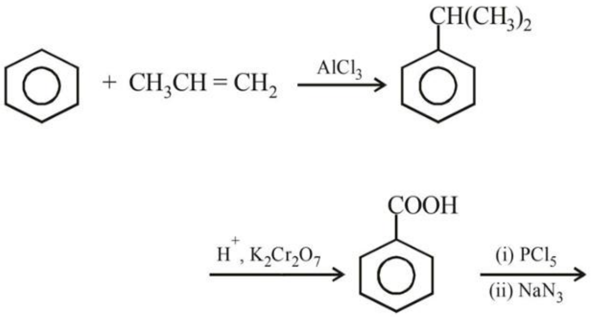
(a)


(b)


(c)


(d)


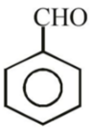
PASSAGE-4

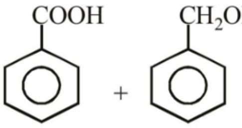


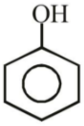
$$C_6H_5CON_3 \xrightarrow{\text{heat}} C_6H_5NCO \xrightarrow{C_2H_5OH} \text{Product}$$

MARK YOUR RESPONSE	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ

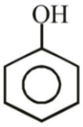
11. What will be the product(s) when isopropylbenzene is oxidised with oxygen and product is acidified

(a)


(b)


(c)


+ CH_3CHO

(d)


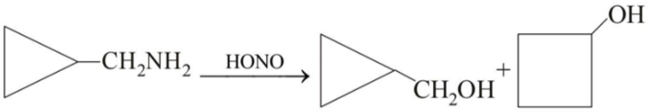
+ $(CH_3)_2C = O$

12. The final product in the above series of reactions is
(a) an amine
(b) a mono substituted urea
(c) a disubstituted urea (d) a urethane

13. Conversion of $C_6H_5CON_3$ to C_6H_5NCO is an example of rearrangement where an alkyl group migrates to
(a) electron deficient carbon atom
(b) electron deficient oxygen atom
(c) electron deficient nitrogen atom
(d) electron rich nitrogen atom

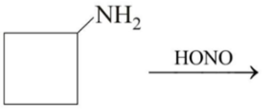
PASSAGE-5

Nitrous acid reacts with amines forming different products depending upon the type of amine. Aliphatic primary amines react with HONO forming alcohol as the major product, other products being alkene and alkyl halide. Certain cyclic primary amines can undergo ring expansion or ring contraction on treatment with HONO again forming alcohol as the major product.

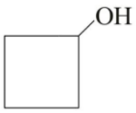


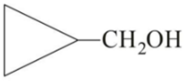
Aromatic primary amines when treated with HONO undergo diazotization to form diazonium salt as the stable product.

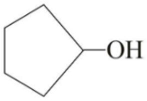
14. Which of the following statement is not true ?
(a) All primary amines first form diazonium salt when treated with nitrous acid.
(b) All aliphatic primary amines when treated with nitrous acid form primary alcohols as the major product
(c) The three classes of amines give different products on treatment with nitrous acid.
(d) None of the three

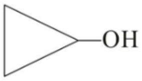
15.


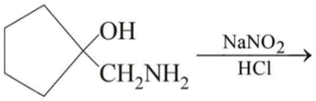
P. Product P may be

(a)


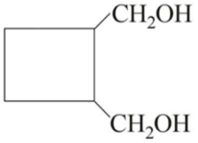
(b)


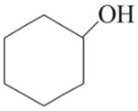
(c)


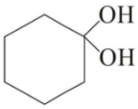
(d)


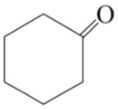
16.


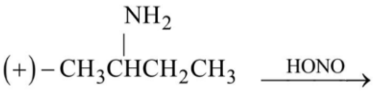
Stable product Z may be

(a)


(b)


(c)


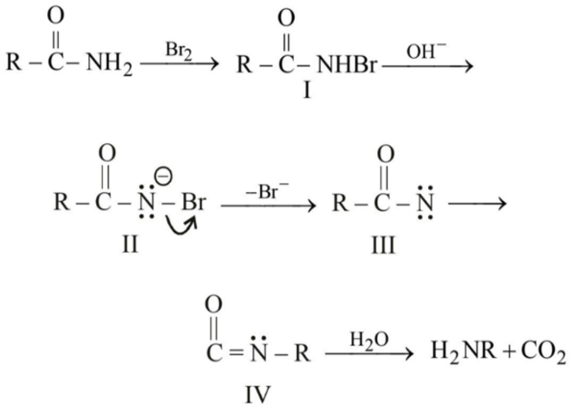
(d)


17.

$(+)-CH_3\overset{NH_2}{\overset{|}{C}}HCH_2CH_3 \xrightarrow{HONO}$ Product is
(a) enantiomer of the original compound
(b) diastereomer of the original compound
(c) racemic mixture of the original compound
(d) (+) – isomer

MARK YOUR RESPONSE	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ
	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ			

PASSAGE-6

Hofmann reaction is found to follow the following path.



18. Number of moles of NaOH used in the complete reaction is

(a) 1 (b) 2

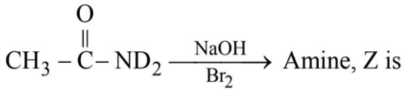
(c) 3 (d) 4

19. Hofmann reaction, when carried out in presence of methanol containing sodium methoxide, instead of NaOH, product is

$$C_6H_5CONH_2 \xrightarrow[CH_3OH]{Br_2, CH_3ONa} \text{Product is}$$

(a) $C_6H_5NH_2$ (b) $C_6H_5NHCOOCH_3$

(c) $C_6H_5NHCH_3$ (d) C_6H_5NHBr

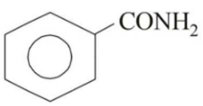
20. 

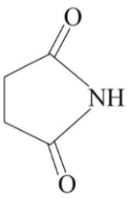
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ND_2 \xrightarrow[Br_2]{NaOH} \text{Amine, Z is}$$

(a) CH_3-ND_2 (b) CH_3NH_2

(c) mixture of (a) and (b) (d) Reaction not possible

***21.** Which of the following will not undergo Hofmann bromamide reaction ?

(a) 

(b) 

(c) $C_6H_5CONHCH_3$ (d) $C_6H_5CONHBr$

22. Which of the following species in the above mechanism is electron deficient ?

(a) I (b) II

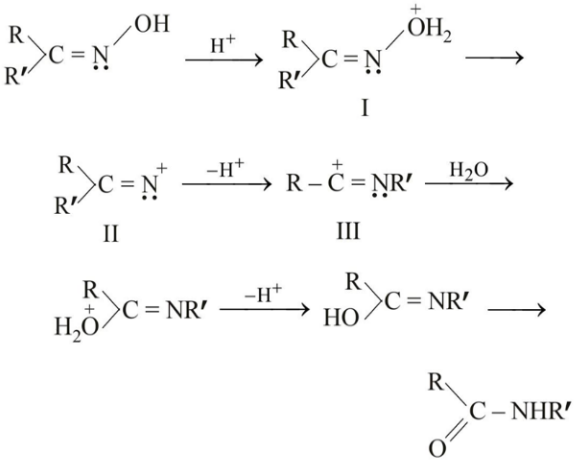
(c) III (d) IV

* In presence of alkali, (b) undergoes hydrolysis to form

$$\begin{array}{l} CH_2CONH_2 \\ | \\ CH_2COO^- \end{array}$$ which when undergoes Hofmann reaction.

PASSAGE-7

Beckmann rearrangement is used for determining the configuration of ketoxines since the two isomers form different N-substituted amides when heated with some acidic reagent. The different steps of the mechanism are as follows.



23. Pick up the species which has an electron deficient centre?

(a) I (b) II

(c) III (d) Two of the three

24. The mechanism involves migration of

(a) R group with its bonding electron pair

(b) R' group with its bonding electron pair

(c) R' group without its bonding electron pair

(d) OH group with its bonding electron pair

25. Which of the following reaction/step is involved in Beckmann rearrangement ?

(a) Formation of conjugated acid

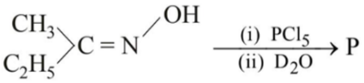
(b) Migration of an alkyl group to electron deficient N

(c) Enlolisation

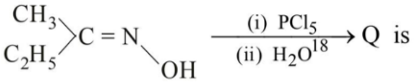
(d) All the three

MARK YOUR RESPONSE	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ
	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ		

26. Predict the product in the following case



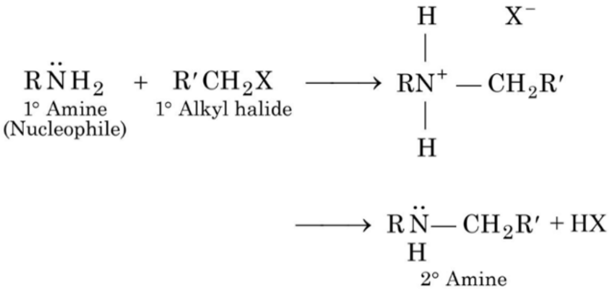
(a) $CH_3CON(D)C_2H_5$ (b) $C_2H_5CON(D)CH_3$
(c) $CH_3CONHC_2H_5$ (d) $C_2H_5CONHCH_3$

27.  Q is

(a) $C_2H_5NHCOCH_3$ (b) $C_2H_5NHCO^{18}CH_3$
(c) $CH_3NHCO^{18}C_2H_5$ (d) $C_2H_5CONHCH_3$

PASSAGE-8

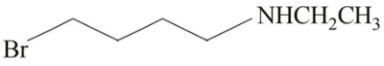
Like ammonia, an amine (1°, 2° or 3°) can react with an alkyl halide to form next higher class of amine. Here, again it is the presence of electron pair on nitrogen which makes amines to behave as nucleophile and alkyl halides thus undergo nucleophilic substitutions.

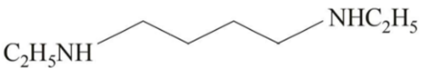


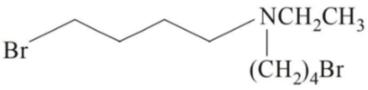
$$\underset{\substack{1^\circ\text{ Amine}\\(\text{Nucleophile})}}{R\ddot{N}H_2} + \underset{1^\circ\text{ Alkyl halide}}{R'CH_2X} \longrightarrow \overset{H\quad X^-}{\underset{H}{RN^+}} - CH_2R' \longrightarrow \underset{2^\circ\text{ Amine}}{\underset{H}{R\ddot{N}} - CH_2R'} + HX$$

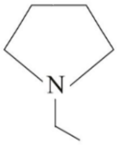
A second alkylation may follow, converting the secondary amine to a tertiary amine which may be alkylated to give a quaternary ammonium salt.

28. Identify the product(s) obtained when $Br(CH_2)_4Br$ is heated with 1 equivalent of ethyl amine

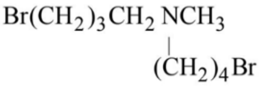
(a) 

(b) 

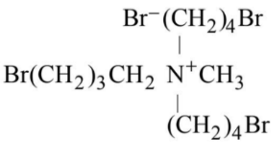
(c) 

(d) 

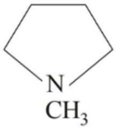
29. Identify the product(s) obtained when $Br(CH_2)_4Br$ is heated with excess of methyl amine

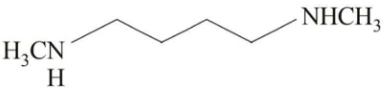
(a) 

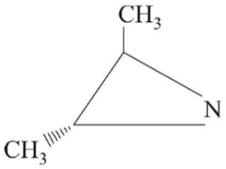
$$Br(CH_2)_3CH_2\underset{(CH_2)_4Br}{NCH_3}$$

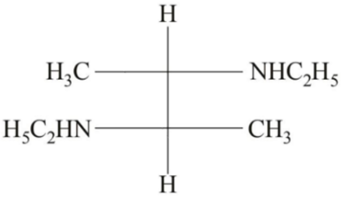
(b) 

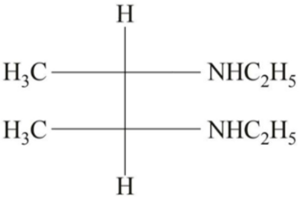
$$Br(CH_2)_3CH_2\overset{Br^-(CH_2)_4Br}{\underset{(CH_2)_4Br}{N^+CH_3}}$$

(c) 

(d) 

30.  $+ C_2H_5NH_2 \longrightarrow Z$, here Z is

(a) 

(b) 

(c) Both of these
(d) None of the two

MARK YOUR RESPONSE	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ

PASSAGE-9

Summary of the four related name reactions for the preparation of primary amines are given below.

$RCONH_2 \xrightarrow{Br_2, OH^-} RNH_2$	Hofmann
$RCON_3 \xrightarrow[heat]{H_2O} RNH_2$	Curtius
$RCONHOH \xrightarrow[H_2O]{OH^-} RNH_2$	Lossen
$RCOOH \xrightarrow[H_2SO_4, OH^-]{HN_3} RNH_2$	Schmidt

31. Reactant of which reaction is not a derivative of carboxylic acid ?
(a) Hofmann (b) Curtius
(c) Lossen (d) None of the three

32. In which of the reactions, leaving group is carboxylate anion?
(a) Hofmann (b) Cutius
(c) Lossen (d) Schmidt

33. In which of the reactions, nitrogen constitutes the leaving group ?
(a) Curtius (b) Schmidt
(c) Both (d) Hofmann

34. Which of the reaction does not require alkaline medium ?
(a) Hofmann (b) Curtius
(c) Schmidt (d) Lossen

35. Which of the reaction is of least importance ?
(a) Schmidt (b) Hofmann
(c) Curtius (d) Lossen

MARK YOUR RESPONSE	31. ⓐⓑⓒⓓ	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ

C REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

(d) Statement-1 is false but Statement-2 is true.

1. **Statement-1** : Sulphanilic acid exists as a dipolar ion whereas *p*-aminobenzoic acid does not.
Statement-2 : Carboxyl group, being more acidic than $-SO_3H$ group, can easily transfer a H^+ to the amino group.

2. **Statement-1** : Nitration of aniline can be conveniently done by protecting the amino group by acetylation.
Statement-2 : Acetylation increases the electron-density in the benzene ring.

3. **Statement-1** : Reduction of *m*-dinitrobenzene with ammonium sulphide gives *m*-nitroaniline.
Statement-2 : *m*-Nitroaniline formed gets precipitated and hence further reduction is prevented.

4. **Statement-1** : Benzonitrile is prepared by the reaction of chlorobenzene with potassium cyanide.
Statement-2 : Cyanide (CN^-) is a strong nucleophile.

5. **Statement-1** : 1° Amides react with Br_2 + NaOH to give 1° amines with one carbon atom less than the parent amide.
Statement-2 : The reaction occurs through intermediate formation of acylnitrene.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

6. **Statement-1** : In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.
Statement-2 : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is no longer available for resonance.

7. **Statement-1** : In order to convert R–Cl to pure R–NH_2, Gabriel-phthalimide synthesis can be used.
Statement-2 : With proper choice of alkyl halides, phthalimide synthesis can be used to prepare 1º, 2º or 3º amines.

8. **Statement-1** : Aniline does not undergo Friedel-Crafts reaction.
Statement-2 : –NH_2 group of aniline reacts with $AlCl_3$ (Lewis acid) to give acid-base reaction.

9. **Statement-1** : Acetamide reacts with Br_2 in presence of methanolic CH_3ONa to form methyl N-methylcarbamate.
Statement-2 : Methyl isocyanate is formed as an intermediate which reacts with methanol to form methyl N-methylcarbamate.

10. **Statement-1** : 1°, 2° and 3° amines are hydrogen-bonding donors, while 1° and 2° amines are hydrogen-bonding acceptors.
Statement-2 : Low molecular weight amines are soluble in water.

11. **Statement-1** : Pyridine is basic.
Statement-2 : Lone pair of electrons on its nitrogen is not involved in aromatic sextet.

12. **Statement-1** : Pyridine is more basic than pyrrole.
Statement-2 : Lone pair of electrons on N in pyridine and pyrrole are different in nature, these form a part of aromatic sextet in pyrrole, while not in pyridine.

13. **Statement-1** : All compounds containing an odd number of nitrogen atoms have odd masses and those containing even number of N atoms have even masses.
Statement-2 : Nitrogen rule can be applied to both aliphatic and aromatic compounds.

14. **Statement-1** : The main product of reaction of alcoholic silver nitrite and ethyl bromide is nitroethane.
Statement-2 : Silver nitrite is predominantly covalent compound.

15. **Statement-1** : HCN on hydrolysis gives formic acid
Statement-2 : HCN is a weak monoprotic acid

16. **Statement-1** : Hofmann elimination gives alkene
Statement-2 : Alkenes are less acidic than NH_3

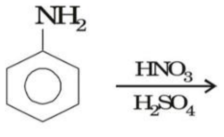
17. **Statement-1** : Nitromethane can give aldol condensation.
Statement-2 : α-Hydrogen of nitromethane is acidic.

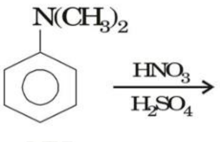
MARK YOUR RESPONSE					
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ
	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ			

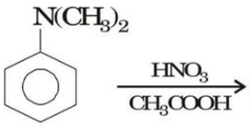
D MULTIPLE CORRECT CHOICE TYPE

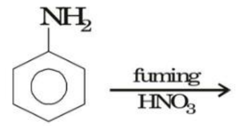
Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. Nitro group can't be introduced easily by which reaction?

(a) 

(b) 

(c) 

(d) 

2. Which of the following compound can be methylated by diazomethane ?
(a) C_2H_5COOH
(b) $C_2H_5NH_2$
(c) C_6H_5OH
(d) $CH_3COCH_2COOC_2H_5$

3. Which of the following amine can be prepared by Gabriel method ?
(*a*) $CH_3CH_2NH_2$
(*b*) $(CH_3)_2CHNH_2$
(*c*) $(CH_3)_3CNH_2$
(*d*) $C_6H_5NH_2$

MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ		

4. Which of the following can't be used as an alkylating agent for an amine ?
(a) CH_3CH_2Cl (b) $CH_2 = CHCl$
(c) C_6H_5Cl (d) $(CH_3)_3CCl$

5. $(CH_3)_3CNH_2$ can't be prepared by
(*a*) reductive amination (*b*) oxime reduction
(*c*) Hofmann degradation (*d*) Gabriel synthesis.

6. Which of the following reaction can be used for preparing aniline ?

(*a*) $C_6H_5COOH \xrightarrow{N_3H,\text{ conc. } H_2SO_4}$

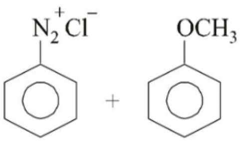
(*b*) $C_6H_5NC \xrightarrow{H_3O^+}$

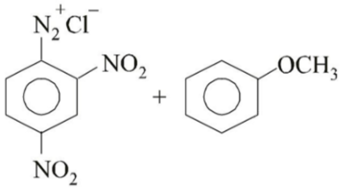
(*c*) $C_6H_5NC \xrightarrow{LiAlH_4}$

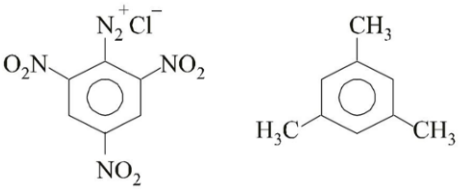
(*d*) $C_6H_5CONH_2 \xrightarrow{Br_2 / NaOH}$

7. Which of the following can exist as inner salt ?
(*a*) *p*-Aminobenzenesulphonic acid
(*b*) *p*-Aminobenzoic acid
(*c*) Aminoacetic acid
(*d*) Alanine

8. Which of the following pairs show coupling reaction ?

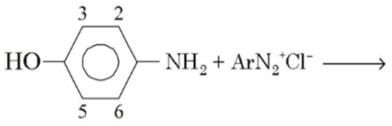
(*a*)


(*b*)


(*c*)


(*d*) Diazotised sulphanilic acid + Dimethylaniline

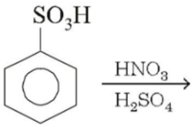
9. Which of the following statement is true regarding reaction of *p*-aminophenol with arenediazonium chloride?

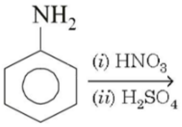


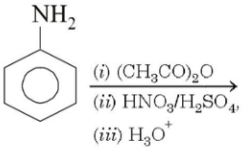
(*a*) Reaction takes place at position 2 in presence of HCl.
(*b*) Reaction takes place at position 3 in presence of NaOH.
(*c*) Only two positions (2 and 6) can be coupled in presence of OH^-
(*d*) Four azo groups can be introduced in the molecule.

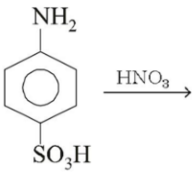
10. Which of the following reacts with nitrous acid ?
(*a*) Acetamide
(*b*) 2-Nitrobutane
(*c*) 2-Methyl-2-nitropropane
(*d*) Diethylamine

11. *p*-Nitroaniline can be obtained by

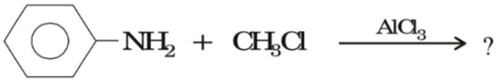
(*a*)


(*b*)


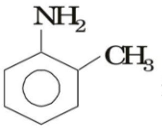
(*c*)


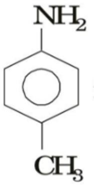
(*d*)


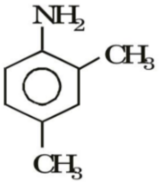
MARK YOUR RESPONSE	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ
	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ		

12. 

Which of the following statement is false regarding above reaction?

(a)  is major product

(b)  is major product

(c)  is major product

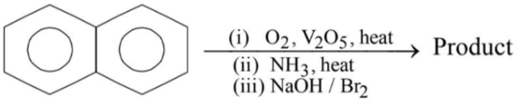
(d) No substitution

13. The correct name for $CH_3N \overset{\rightarrow}{\equiv} C$ is

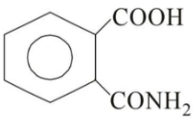
(a) methyl carbylamine	(b) methyl isocyanide
(c) methyl isonitrile	(d) acetoisonitrile

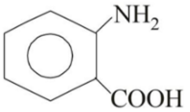
14. Urea on heating with ethyl alcohol gives

(a) urethane	(b) semicarbazide
(c) malonylurea	(d) ethyl carbonate

15. 

Which of the following statement (s) is (are) true regarding above series of reactions ?

(a) Product formed is 

(b) Product formed is 

(c) Reaction involved is oxidation

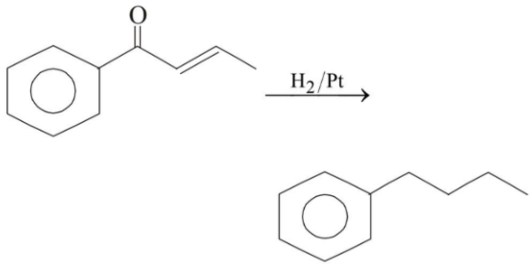
(d) Reaction involved is Hofmann degradation

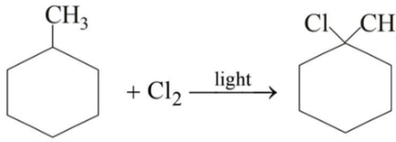
16. Oximes can be converted into amides by

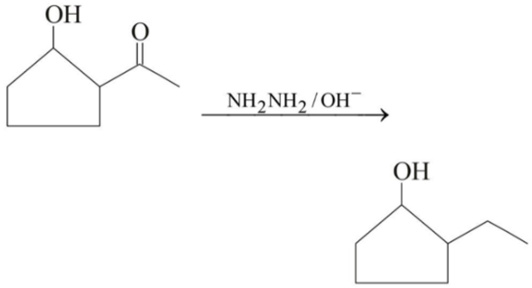
(a) SO_3	(b) BF_3
(c) PCl_5	(d) $C_6H_5SO_2Cl$

17. Pick up the correct statement

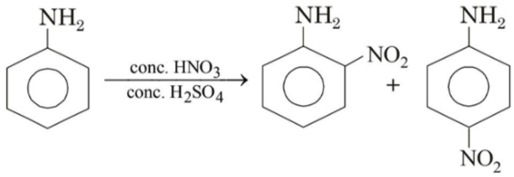
(a) Toluene and ethane, both react at the same rate with chlorine in presence of light.

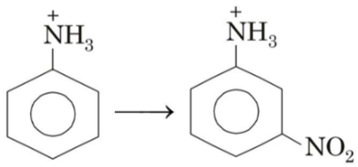
(b) 

(c) 

(d) 

18. Which of the following is/are correct regarding nitration of aniline with conc HNO_3 and conc. H_2SO_4 ?

(a) 

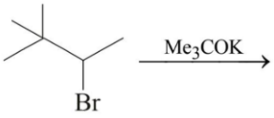
(b) 

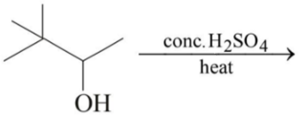
(c) The substitution can be explained on the basis of inductive effect (– I)

(d) The substitution can be influenced by +M and +E effects.

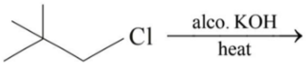
Mark Your Response	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ
	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ			

19. In which of the following reaction, Hofmann elimination is the major product ?

(a) 

(b) 

(c) 

(d) 

20. Which of the following intermediates are likely to be formed when 2-methylpropyl amine is treated with nitrous acid ?

(a) $(CH_3)_2CH\overset{+}{C}H_2$ (b) $(CH_3)_3C\overset{+}{O}H_2$

(c) $(CH_3)_2CHCH_2\overset{+}{O}H_2$ (d) $(CH_3)_2\overset{+}{C}CH_3$

21. Carbenes are the reactive intermediates in

(a) Reimer Tiemann reaction

(b) Wittig reaction

(c) Hofmann bromamide reaction

(d) Carbylamine reaction

22. Which of the following are intermediates in Sandmeyer reaction ?

(a) $C_6H_5N^+ \equiv NCl^-$ (b) $C_6H_5N^+ \equiv N$

(c) $\dot{C}_6H_5$ (d) C_6H_5Cl

23. $\underset{(X)}{C_4H_{11}N} + HONO \longrightarrow \underset{(3° \text{ alcohol})}{C_4H_{10}O}$

X should

(a) give carbylamine reaction

(b) undergo diazotisation

(c) react with water

(d) give Hofmann bromamide reaction

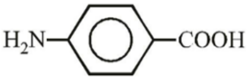
MARK YOUR RESPONSE	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ

E MATRIX-MATCH TYPE

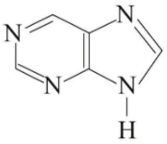
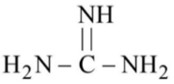
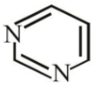
Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A–p, s and t; B–q and r; C–p and q; and D–s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	●	○	○	●	●
B	○	●	●	○	○
C	●	●	○	○	○
D	○	○	○	●	○

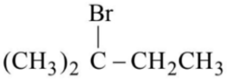
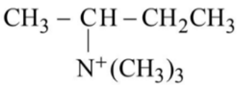
1.

	Column-I		**Column-II**
(A)	Hydrogen bonding	p.	Ethyl acetoacetate
(B)	β-Amino acids	q.	Proteins
(C)		r.	Zwitterion
(D)	Aniline	s.	Diazotisation

2.

	Column-I		**Column-II**
(A)		p.	One type of N
(B)	 $H_2N-\overset{NH}{\overset{\Vert}{C}}-NH_2$	q.	Two types of N
(C)		r.	Aromatic
(D)	$C_6H_5N^+\equiv NCl^-$	s.	Non-aromatic

3.

	Column-I		**Column-II**
(A)	$CHCl_3 \xrightarrow{OH^-}$	p.	Hofmann product
(B)	$CHCl_2-CF_3 \xrightarrow{OC_2H_5^-}$	q.	E2 mechanism
(C)	 $(CH_3)_2\overset{Br}{\overset{\vert}{C}}-CH_2CH_3 \xrightarrow{Me_3CO^-}$	r.	α-Elimination
(D)	 $CH_3-\underset{N^+(CH_3)_3}{\underset{\vert}{CH}}-CH_2CH_3 \xrightarrow{OH^-}$	s.	E1cB

4.

	Column-I		**Column-II**
(A)	ArS_{N_1} as intermediate	p.	Carbocation
(B)	ArS_{N_2} as intermediate	q.	Carbanion
(C)	$OH^- > (CH_3)_3CO^-$	r.	Basic character
(D)	$OH^- < NH_2^-$	s.	Nucleophilic character

5.

	Column-I		**Column-II**
(A)	Allylic rearrangement	p.	Carbanions
(B)	Hofmann rearrangement	q.	Electron deficient species
(C)	Wittig reaction	r.	Carbocations
(D)	Carbylamine reaction	s.	Carbenes

6.

	Column-I		**Column-II**
(A)	Gabriel phthalimide reaction	p.	$C_6H_5CH_2NH_2$
(B)	Reduction with $LiAlH_4$	q.	$C_6H_5NH_2$
(C)	Reaction with alc. $KOH + CHCl_3$	r.	C_6H_5CN
(D)	1° Amide with $Br_2 + KOH$	s.	$CH_3CH_2NH_2$

MARK YOUR RESPONSE

1.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

2.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

3.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

4.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

5.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

6.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

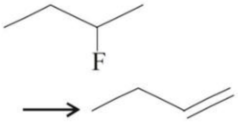
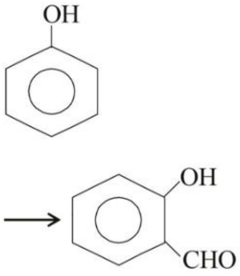
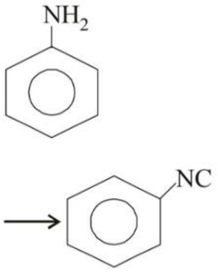
7.

	Column I		*Column II*
(A)	Pyrolysis of quaternary ammonium salts	p.	*syn*-Elimination
(B)	β-Dehydrohalogenation	q.	*anti*-Elimination
(C)	γ-Dehydrohalogenation	r.	Saytzeff product
(D)	Dehydration of alcohol	s.	Hofmann product

8.

	Column I		*Column II*
(A)	Normal base with 1° alkyl fluoride	p.	E1 reaction
(B)	Normal base with 2° alkyl chloride	q.	E2 reaction
(C)	Bulkyl base with 1° alkyl halide	r.	Saytzeff product
(D)	Dehydration of alcohol	s.	Hofmann product

9.

	Column I		*Column II*
(A)		p.	$CHCl_3$ / alc. KOH
(B)	$CH_2 = CHCl \longrightarrow CH \equiv CH$	q.	$:CCl_2$
(C)		r.	$NaNH_2$
(D)		s.	C_2H_5OH / KOH

10.

	Column - I		**Column - II**
(A)	Hofmann degradation	p.	Amides
(B)	Beckmann rearrangement	q.	Isocyanates
(C)	Curtius rearrangement	r.	$NaOH/Br_2$
(D)	Lossen rearrangement	s.	$RCON_3$

MARK YOUR RESPONSE

7.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

8.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

9.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

10.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

Answerkey

A SINGLE CORRECT CHOICE TYPE

1.	(b)	**7.**	(a)	**13.**	(c)	**19.**	(b)	**25.**	(b)	**31.**	(a)	**37.**	(b)	**43.**	(c)	**49.**	(d)
2.	(c)	**8.**	(d)	**14.**	(b)	**20.**	(d)	**26.**	(d)	**32.**	(b)	**38.**	(d)	**44.**	(b)	**50.**	(c)
3.	(b)	**9.**	(b)	**15.**	(b)	**21.**	(b)	**27.**	(c)	**33.**	(d)	**39.**	(c)	**45.**	(d)	**51.**	(c)
4.	(a)	**10.**	(d)	**16.**	(c)	**22.**	(a)	**28.**	(d)	**34.**	(c)	**40.**	(b)	**46.**	(d)	**52.**	(a)
5.	(d)	**11.**	(c)	**17.**	(d)	**23.**	(b)	**29.**	(d)	**35.**	(d)	**41.**	(c)	**47.**	(c)	**53.**	(b)
6.	(a)	**12.**	(d)	**18.**	(d)	**24.**	(b)	**30.**	(c)	**36.**	(c)	**42.**	(d)	**48.**	(c)	**54.**	(b)

B COMPREHENSION TYPE

1	(b)	**7**	(c)	**13**	(c)	**19**	(b)	**25**	(d)	**31**	(d)
2	(d)	**8**	(c)	**14**	(b)	**20**	(b)	**26**	(c)	**32**	(c)
3	(b)	**9**	(d)	**15**	(a,b)	**21**	(c)	**27**	(c)	**33**	(c)
4	(c)	**10**	(a)	**16**	(d)	**22**	(c)	**28**	(a, d)	**34**	(b)
5	(a)	**11**	(d)	**17**	(c)	**23**	(d)	**29**	(c,d)	**35**	(d)
6	(c)	**12**	(d)	**18**	(d)	**24**	(b)	**30**	(a)		

C REASONING TYPE

1	(c)	**4**	(d)	**7**	(c)	**10**	(b)	**13**	(b)	**16**	(b)
2	(c)	**5**	(a)	**8**	(a)	**11**	(a)	**14**	(a)	**17**	(a)
3	(c)	**6**	(d)	**9**	(a)	**12**	(a)	**15**	(d)		

D MULTIPLE CORRECT CHOICE TYPE

ANSWER KEY											
1.	(a,b,d)	**5.**	(a,b,d)	**9.**	(a,b,d)	**13.**	(a,b,d)	**17.**	(c,d)	**21.**	(a,b,d)
2.	(a,c,d)	**6.**	(a,b,d)	**10.**	(a,b,d)	**14.**	(a,d)	**18.**	(b,c)	**22.**	(b,c)
3.	(a,b)	**7.**	(a,c,d)	**11.**	(c,d)	**15.**	(b,c,d)	**19.**	(a,c)	**23.**	(a,b,c)
4.	(b,c,d)	**8.**	(b,c,d)	**12.**	(a,b,c)	**16.**	(a,b,c)	**20.**	(b,d)		

E MATRIX-MATCH TYPE

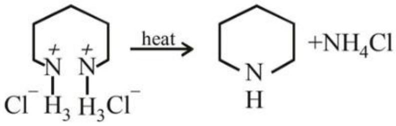
1. **A-p, q; B-r, s; C-r, s; D-s**
2. **A-q, r; B-p, s; C-p, r; D-p, r**
3. **A-r; B-s; C-p, q; D-p, q**
4. **A-p; B-q; C-s; D-r**
5. **A-q, r; B-q; C-p; D-q, s**
6. **A-p, s; B-p, s; C-p, q, s; D-p, q, s**
7. **A-s; B-q, r, s; C-p; D-r**
8. **A-q, s; B-q, r; C-q, s; D-p, r**
9. **A-r, s; B-r; C-p, q; D-p, q**
10. A-p, q, r; B-p; C-q, s; D-q

Solutions

A SINGLE CORRECT CHOICE TYPE

1. **(b)** $LiAlH_4$ does not reduce $-NO_2$ group to $-NH_2$ group.

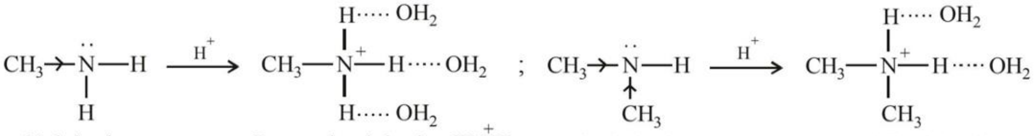
2. **(c)**



3. **(b)** Amalgamated -Zn and HCl reduces carbonyl group to methylene group without affecting the double bond. However, Zn and HCl reduces $-NO_2$ to $-NH_2$ group.

4. **(a)** In amines, N is sp^3 hybridised and thus has pyramidal shape. In the given structure, since the three alkyl groups are different, and the fourth corner of the pyramid is occupied by lone pair of electrons, the molecule is chiral. However, the two enantiomers of the amine are not resolvable because of their rapid interconversion through a transition state having planar structure (sp^2 hybridised nitrogen)

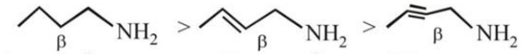
5. **(d)** The basic character of an amine in water is determined by (i) electron availability on the N atom and (ii) the extent of stabilization of the cation (protonated amine) due to solvation by hydrogen bonding



Methyl amine; Protonated methyl amine, $CH_3\overset{+}{N}H_3$ (Highly stabilized); Dimethyl amine; Protonated dimethyl amine (Lesser stabilized than $CH_3\overset{+}{N}H_3$)

6. **(a)** In presence of chlorobenzene, hydrogen bonding is not possible between the protonated amine and the solvent and thus the stabilization factor (solvation effect) is absent. Hence basicity is explained on the basis of the number of electron releasing groups in an amine.

7. **(a)** Note the point of difference in the given compounds which here lies at β-carbon. In I, II, III, the β-carbon atoms are sp^3, sp^2 and sp hybridised respectively which in turn cause the difference in their *s* character. We know that more is the *s* character of an atom, greater will be its electron-withdrawing nature. Thus sp (50% *s* character) hybridised carbon is most electron-withdrawing, while sp^3 (25% *s* character) is least electron-withdrawing. Further, we know that presence of an electron-withdrawing group decreases basicity of an amine. Thus

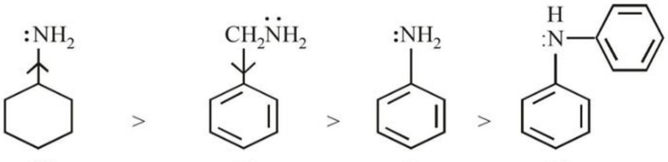


I (β – C sp^3 hybridised) > II (β – C sp^2) > III (β – C sp)

8. **(d)** Here again the two amines differ in the nature of β-carbon atom

II > I

9. **(b)** Greater the delocalisation of electron pair on N, lesser is its availability for protonation leading to lesser basic character.



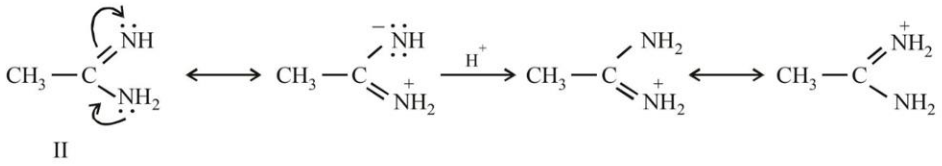
IV > II > I > III

IV: Delocalisation not possible, cyclohexyl gp. is electron-releasing

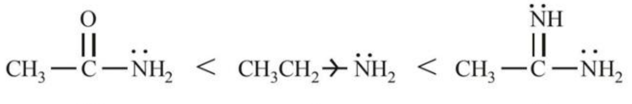
II: Delocalisation not possible, phenyl gp. is electron-withdrawing

I, III: Delocalisation possible, more in III than in I. Further C_6H_5- gp. is electron-withdrawing

10. (d) II is most basic because delocalisation of electron pair leads to negative charge on N making it electron-rich and hence liable to be attacked by proton very easily. Moreover, the corresponding protonated species is very much stable because of equivalent contributing structures.



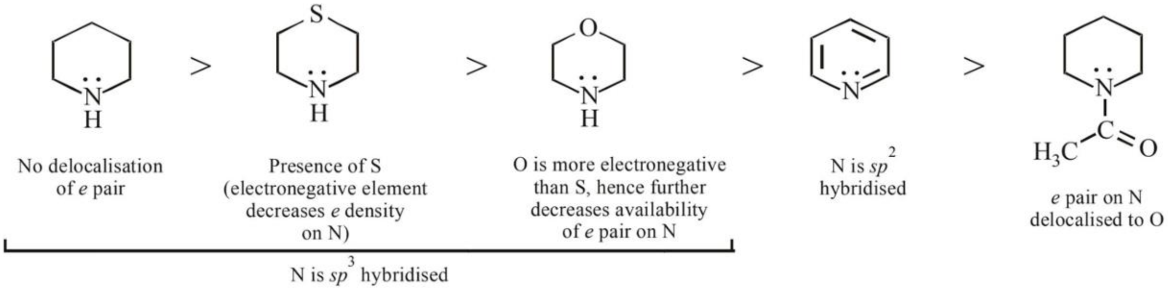
Species III is least basic because of delocalisation of electron pair on N, making it less available for protonation. Species I lies in mid-way, thus



$CH_3-CO-\ddot{N}H_2 < CH_3CH_2\rightarrow\ddot{N}H_2 < CH_3-C(=\ddot{N}H)-\ddot{N}H_2$

III I II

11. (c)



No delocalisation of *e* pair

Presence of S (electronegative element decreases *e* density on N)

O is more electronegative than S, hence further decreases availability of *e* pair on N

N is *sp*^{2} hybridised

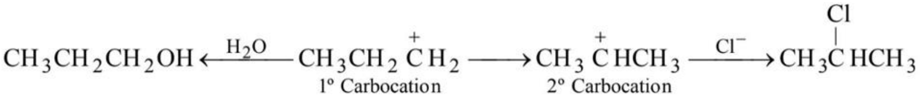
e pair on N delocalised to O

N is *sp*^{3} hybridised

12. **(d)** In presence of $AlCl_3$ (a Lewis acid), aniline is converted into anilinium cation, which being *m*-directing gives *m*-aminoacetophenone.

13. **(c)** Although aliphatic 1º amines form diazonium salts, these are unstable and decompose to alkyl carbocation which can form variety of normal as well as rearranged products.

$$CH_3CH_2CH_2NH_2 \xrightarrow[0°C]{HONO} \Big[\underset{\text{Unstable}}{CH_3CH_2CH_2N_2^+Cl^-}\Big] \rightarrow CH_3CH_2\overset{+}{C}H_2 + N_2 + Cl^-$$



$$CH_3CH_2CH_2OH \xleftarrow{H_2O} \underset{\text{1º Carbocation}}{CH_3CH_2\overset{+}{C}H_2} \longrightarrow \underset{\text{2º Carbocation}}{CH_3\overset{+}{C}HCH_3} \xrightarrow{Cl^-} CH_3\overset{Cl}{\overset{|}{C}}HCH_3$$

14. **(b)** Couplings of arenediazonium cations and phenols take place most rapidly in slightly alkaline medium because

(i) acidic medium (pH < 7) will suppress the ionisation of C_6H_5OH to the more reactive $C_6H_5O^-$, while the alkaline medium (pH > 7) will enhance ionisation of phenol to phenoxide ion.

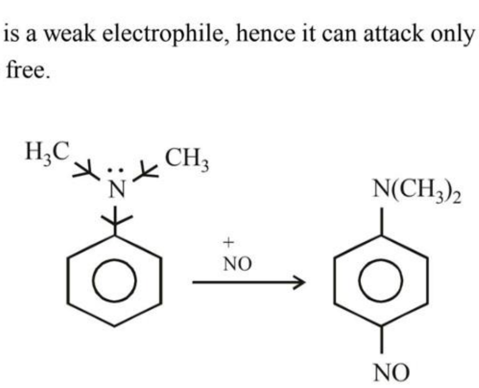
(ii) strongly alkaline medium (pH > 10) causes the arenediazonium salt to react with the OH^- ion to form a relatively unreactive diazohydroxide or diazoate ion.

$$Ar\overset{+}{N}\equiv\ddot{N} \underset{}{\overset{OH^-}{\rightleftharpoons}} \underset{\text{Diazohydroxide}}{Ar-\ddot{N}=\ddot{N}-\ddot{O}H} \overset{OH^-}{\rightleftharpoons} \underset{\text{Diazoate ion}}{Ar-\ddot{N}=\ddot{N}-\ddot{O}\!:^-}$$

15. **(b)** Reaction is an example of **Schmidt reaction** in which carboxylic acids are heated with hydrazoic acid in presence of a mineral acid to form primary amines.

$$RCOOH + HN_3 \xrightarrow{\text{conc. } H_2SO_4} RNH_2 + CO_2$$

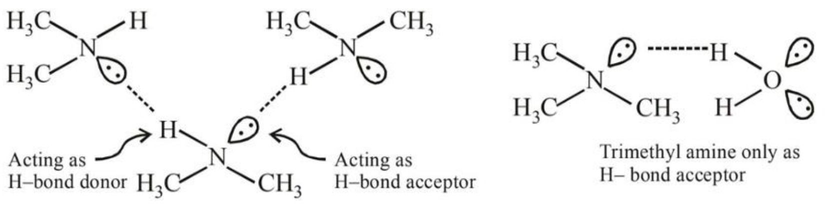
16. **(c)** Nitrosonium ion, $\overset{+}{N}O$ from HONO is a weak electrophile, hence it can attack only on highly activated benzene nucleus, provided proper position, *p*- or *o*- is free.



17. **(d)** $LiAlH_4$ does not reduce $-NO_2$ group.

18. **(d)** Most of the simple amines those having smaller alkyl (groups) can't be resolved , although they may contain three different alkyl groups.

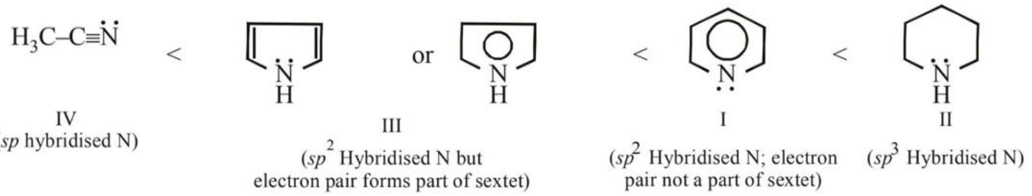
19. **(b)** Hydrogen bonding is a strong intermolecular attraction between an electrophilic O–H or N–H hydrogen atom and a pair of non-bonding electrons. Thus a hydrogen bond requires both a **hydrogen bond donor** (a molecule having O–H or N–H group) and a **hydrogen bond acceptor** (a molecule having lone pair of electrons). Thus dimethyl amine can serve as hydrogen bond donor due to N–H group as well as hydrogen bond acceptor due to lone pair of electrons on N. Such molecules can form hydrogen bond with themselves and also with water (or other hydrogen bond donor). On the other hand, trimethyl amine can serve only as hydrogen bond acceptor since it has lone pair of electrons but not hydrogen on N. Hence it can form hydrogen bond with water but not with themselves.



20. **(d)** Nearly all amines have unpleasant odour, while their salts are odourless, Amines having more than 6 carbon atoms are insoluble in water while their salts are soluble in water, hence the latter can be easily converted into syrup. Amines are susceptible to oxidation because of presence of lone pair of electrons on N.

21. **(b)** Cold dil. NaOH does not attack to either of the compound, while cold dil. HCl reacts only with benzyl amine $C_6H_5CH_2NH_2$.

22. **(a)** The four compounds differ in two respects : Compounds II has sp^3 hybridised N, compounds I and III have sp^2 while compound IV has *sp* hybridised N. Now we know that greater the *s* character of an orbital, more tightly its electrons are held and hence lesser will be their availability for protonation causing weak basic character. Thus the basic character of the three N's is $sp^3N > sp^2 N > sp N$. However, in pyrrole electrons on N are part of aromatic sextet, i.e., these are delocalised and hence lesser available for protonation and thus pyrrole is a weaker base than pyridine because in pyridine nonbonding electrons present in sp^2 orbital do not form a part of aromatic sextet. Thus the basic character should be in the following order.

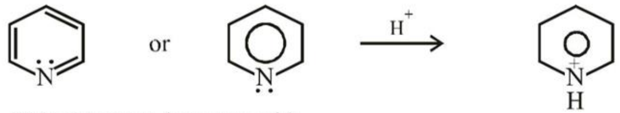


23. **(b)** Explained in the above question.

24. **(b)**


I (Sextet present, hence aromatic) (*e* pair on N forms a part of aromatic sextet)

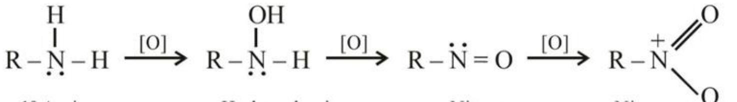
II (not aromatic) (Aromatic sextet is not present because *e* pair is involved in protonation)


III (sextet present, hence aromatic) (*e* pair on N, not a part of sextet)

IV (sextet present, hence aromatic)

25. **(b)** This is an example of Hofmann elimination which generally takes place by E2 mechanism and the latter requires a strong base (recall that OH^- is a strong base than I^-). The NH_2^-, being a strong base, can't be eliminiated easily.

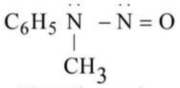
26. **(d)** All of the three are oxidation produces of a 1° amine.

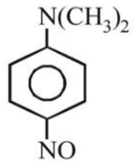

1° Amine Hydroxylamine Nitroso Nitro

27. **(c)** Cope elimination is used for removing a nitrogen present outside the ring, while Hofmann elimination is used for removing nitrogen present inside as well as outside the ring.

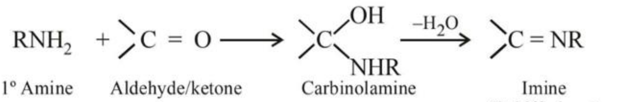
28. **(d)** All the three react with HONO forming following respective products.

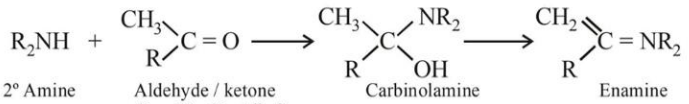
$C_6H_5\overset{+}{N}\equiv NCl^-$
Diazonium chloride


$C_6H_5\ddot{N}(CH_3)-\ddot{N}=O$
2° N–Nirosoamine


p- Nitrosodimethylamine

29. **(d)**


1° Amine Aldehyde/ketone Carbinolamine Imine (Schiff's base)

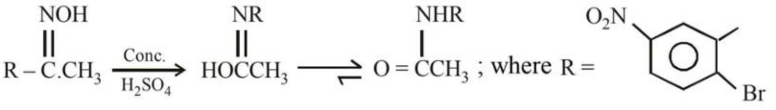

2° Amine Aldehyde / ketone (R = H) (R=Alkyl) Carbinolamine Enamine

30. **(c)** Pyridine resembles a strongly deactivated benzene, here the deactivation is due to electron-withdrawing effect of the electrongative N atom from 2-and 4 - positions making 3-positions to be more vulnerable for the attack of an electrophile. Remember that the nonbonding electrons on N are perpendicular to the π-system (they are present in sp^2 orbital), these are not involved in delocalisation, i.e., they can't stabilize the positively charged intermediate.

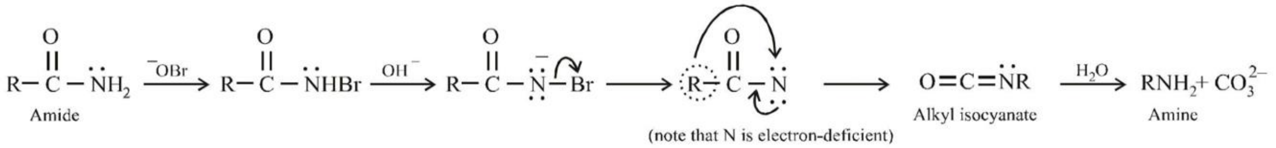
31. **(a)** Due to greater electronegativity of N over S, positive charge on N will make the methyl groups more electron- deficient than that on positively charged S. Therefore, $(CH_3)_4N^+I^-$ will undergo nucleophilic substitution more readily than the sulphur analogue.

$$HO^- + CH_3 \rightarrow N^+(CH_3)_3 \longrightarrow CH_3OH + (CH_3)_3N$$

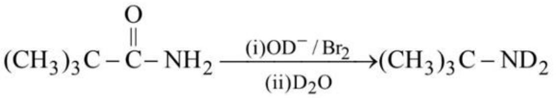
32. **(b)** It is an example of Beckmann rearrangment ; where the group *anti* to –OH migrates



33. **(d)** For this one should remember that Hofmann's degradation involves migration to electron deficient nitrogen atom, hence the alkyl group will migrate with its bonding pair of electrons.



34. **(c)** Remember that in Hofmann rearrangement, the two original H atoms of the –CONH$_2$ group are removed by base (OH$^-$) and new H's are derived from H_2O.

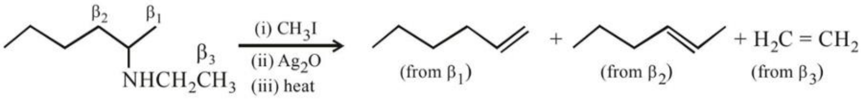


$$(CH_3)_3C-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow[(ii)D_2O]{(i)OD^-/Br_2} (CH_3)_3C-ND_2$$

35. **(d)** $HCCl_3 \xrightarrow{OH^-} :\bar{C}Cl_3 \xrightarrow{-Cl^-} :CCl_2$

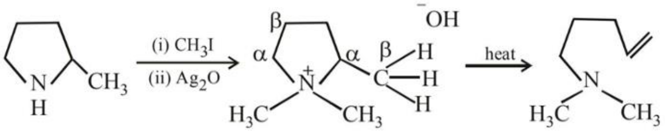
Dichlorocarbene
(a neutral electron deficient species)

36. **(c)** The given amine has three β-hydrogens, hence it can form three alkenes of which least substituted ($H_2C{=}CH_2$) will be the major product (Hofmann product or Hofmann elimination).

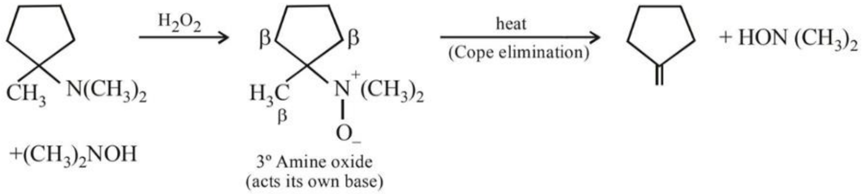


In Hofmann elimination H atom (in the form of proton) is eliminated from that β carbon atom which has maximum number of H atom(s). This is due to the fact that Hofmann elimination (an example of E2 reaction) requires anti-coplanar arrangement of the β H atom and the leaving group. Further, higher the chances for this arrangement to remain in staggered conformation more will be the ease of elimination. Thus greater the number of H atom at β position, higher will be the chances for Me_3N^+– and H atom to remain in this particular conformation (anti-coplanar arragnement of Me_3N^+– and H atom in staggered conformation).

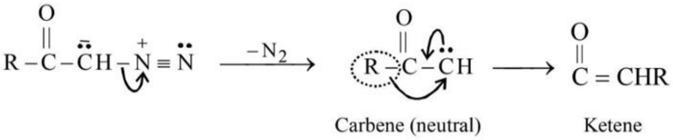
37. **(b)**



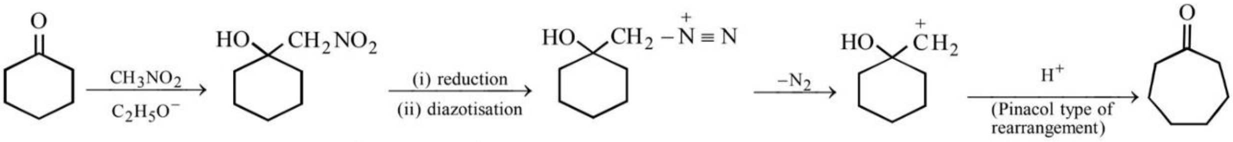
38. **(d)** The reaction involves Cope eliminiation (heating of a 3° amine oxide to form an alkene with the elimination of a 2° hydroxylamine).



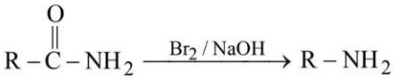
39,40. **(c)**, **(b)**

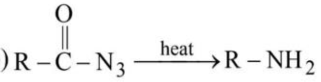


41. **(c)**

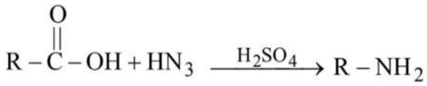


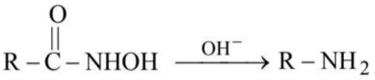
42. **(d)** All the three reactions lead to the formation of C = C bonds under usual conditions.

43. **(c)** (a) 
$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2/NaOH} R-NH_2$ **(Hofmann reaction)**

(b) 
$R-\overset{O}{\overset{\|}{C}}-N_3 \xrightarrow{heat} R-NH_2$ **(Curtius reaction)**

Azide

(c) 
$R-\overset{O}{\overset{\|}{C}}-OH + HN_3 \xrightarrow{H_2SO_4} R-NH_2$ **(Schmidt reaction)**

(d) 
$R-\overset{O}{\overset{\|}{C}}-NHOH \xrightarrow{OH^-} R-NH_2$ **(Lossen reaction)**

Hydroxamic acid

44. **(b)** $R-N=C=O$ (Alkyl isocyanate) is the common intermediate in the four reactions.

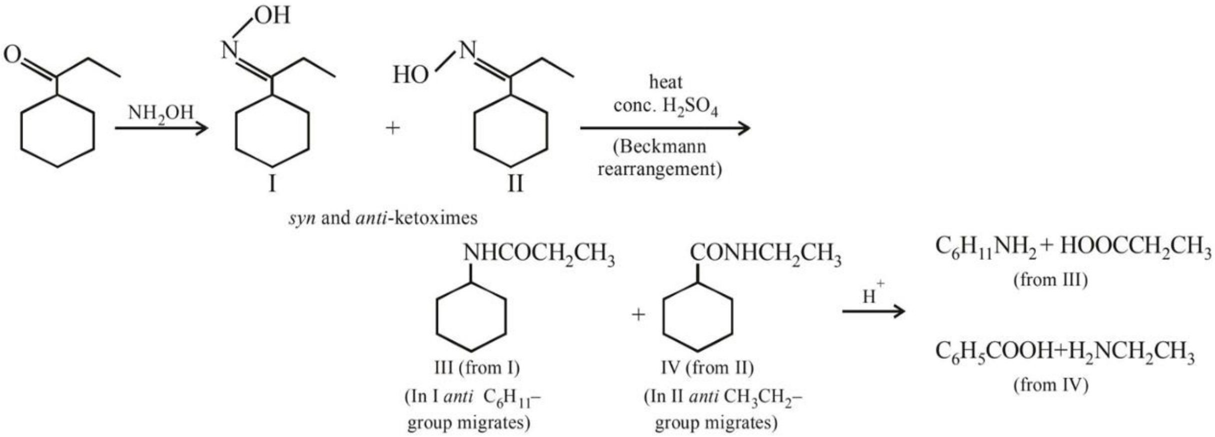
45. **(d)** In other three, the group migrates to electron deficient carbon.

46. **(d)** All the three are formed.

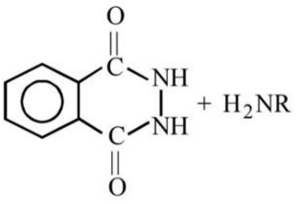
47. **(c)** $CH_3NH_2 \xrightarrow[excess]{CH_3I} \underset{(A)}{(CH_3)_4N^+I^-} \xrightarrow{AgOH} \underset{(B)}{(CH_3)_4N^+OH^-} \xrightarrow{heat} \underset{(C)\ and\ (D)}{(CH_3)N + CH_3OH}$

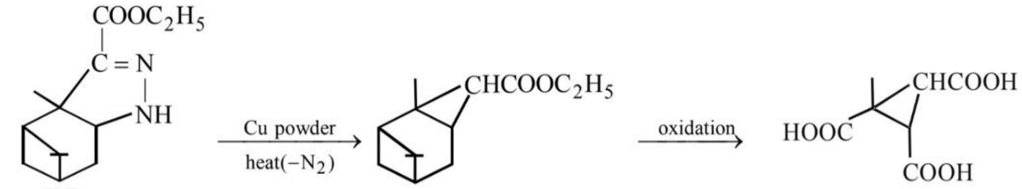
48. **(c)** $CH_3COOH \xrightarrow[(ii)\ PBr_3]{(i)\ LiAlH_4} CH_3CH_2Br \xrightarrow[(ii)\ LiAlH_4]{(i)\ KCN} CH_3CH_2CH_2NH_2 \xrightarrow{CHCl_3, OH^-}$

$CH_3CH_2CH_2NC \xrightarrow[(+2H_2O)]{hydrolysis} CH_3CH_2CH_2NH_2 + HCOOH$

49. **(d)** 

50. **(c)** The reaction is an example of hydrazinolysis.



51. **(c)** 

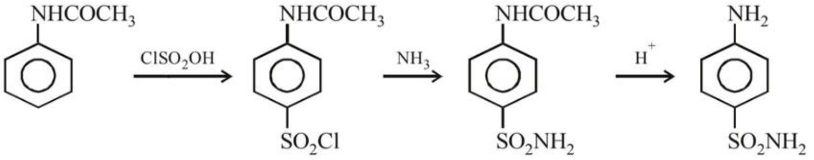
[Y]
Pyrazoline derivative

[Z]

B COMPREHENSION TYPE

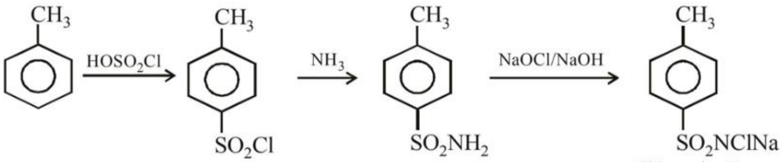
1. **(b)** E2 eliminations are concreted and *anti*-stereoselective.
2. **(d)** Due to the bulk of the $-N^+Me_3$ group, the OH^- preferentially approaches and removes the least hindered β-hydrogen and thus form the least substituted alkene as the major product (difference from Saytzeff product).
3. **(b)** Species II (acylnitrene) is electron-deficient (N has only 6 electrons), hence it has a tendency to get its octet completed by the migration of alkyl group.
4. **(c)** $-OCH_3$ is more electron-releasing hence when the migrating aryl group has $-OCH_3$ in the para postion, its migration is accelerated.
5. **(a)** The migrating group (the group attached to C of the $-CONH_2$ part) never becomes free, so optical activity of the reactant is maintained.
6. **(c)** Since phenyl group (migrating group) does not become free, no cross product [i.e., (ii) and (iv)] is formed.

7–8–9.(c–c–d) **Reaction (i)**



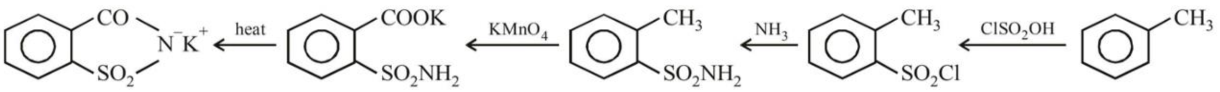
Sulphanilamide
(a sulpha drug)

Reaction (ii)

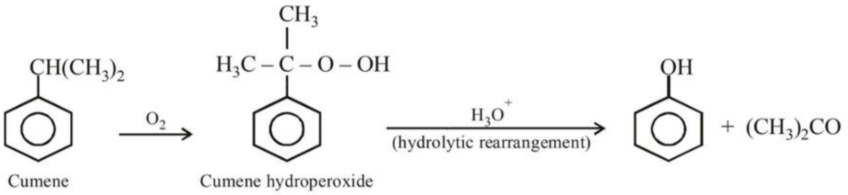


Chloramine T
(an artificial sweetner)

10. **(a)** Going backward, we can obtain answer



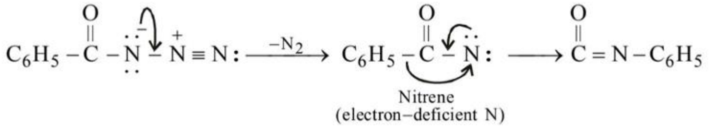
11. **(d)**



This step involves migration of phenyl group to electron-deficient oxygen.

12. **(d)** $C_6H_5-N=C=O \xrightarrow{C_2H_5OH} \underset{\text{Urethane}}{C_6H_5-NHCOOC_2H_5}$

13. **(c)**



$$C_6H_5-\overset{O}{\overset{\|}{C}}-\ddot{\underset{..}{N}}^{-}-\overset{+}{N}\equiv N: \xrightarrow{-N_2} \underset{\substack{\text{Nitrene}\\ \text{(electron–deficient N)}}}{C_6H_5-\overset{O}{\overset{\|}{C}}-\ddot{N}:} \longrightarrow \overset{O}{\overset{\|}{C}}=N-C_6H_5$$

C REASONING TYPE

1. **(c)** The correct reason is : $-SO_3H$ group, being more acidic than $-CO_2H$ group, can easily transfer a proton to the amino group.
2. **(c)** The correct reason is : Acetylation decreases the electron-density in the benzene ring thereby preventing oxidation.

3. **(c)** The correct reason is : The overall electron deficiency in *m*-nitroaniline is much less (due to –R-effect of NO_2 group and +R-effect of NH_2 group) than in *m*-dinitrobenzene (–R-effect of the two NO_2 groups) and hence does not accept additional electrons from a weak reducing agent such as $(NH_4)_2S$ and thus further reduction is prevented.

4. **(d)** Aryl halides (chlorobenzene) do not undergo nucleophilic substitution with KCN because of the low reactivity of the Cl atom, which is because of resonance in chlorobenzene. So assertion is wrong. Reason is correct.

5. **(a)** **R** is the correct explanation of **A**.

6. **(d)** In strongly acidic conditions, aniline becomes protonated with the result lone pair of electrons is not available to produce +E and +M effects. On the other hand, the $-\overset{\oplus}{N}H_3$ group exerts strong –I effect causing deactivation of the ring.

7. **(c)** **Correct R :** Only primary aliphatic amines can be prepared by Gabriel phthalimide reaction.

8. **(a)** **R** is the correct explanation of **A**.

9. **(a)** **R** is the correct explanation of **A**.

D MULTIPLE CORRECT CHOICE TYPE

1. **(a,b,d)** Tertiary amino group is a strong activator, nitration can be carried out under milder conditions ($HNO_3 + CH_3COOH$). In Tertiary amines, electron pair on N is shielded by two bulky methyl groups, so these are not easily oxidised by mild oxidising agents.

2. **(a,c,d)** Diazomethane is used for methylating acidic groups ; compound IV has enolic —OH group, hence it can also be methylated by CH_2N_2.

3. **(a,b)** For the preparation of Me_3CNH_2, the required alkyl halide is Me_3CX which will react with potassium phthalimide, a strong base, to form alkene rather than substituted product. For preparing $C_6H_5NH_2$, C_6H_5Cl will be the starting halide in which Cl is non-reactive.

4. **(b,c,d)** Vinyl and aryl halides do not undergo S_{N^2} reactions, unless activated by electron withdrawing group (in the *o*- and *p*-position in case of aryl halides). 3° Halides form alkenes on elimination.

5. **(a,b,d)** In **reductive amination method**, products can have only CH_3, a 1°C, or 2°C bonded to N as in CH_3NH_2, RCH_2NH_2 or R_2CHNH_2 respectively. In the **reduction of oxime**, amine formed can have only 1° or 2°C bonded to N. In **Gabriel phthalimide method**, the required Me_3CCl would undergo elimination (E2) rather than substitution (S_{N^2}).

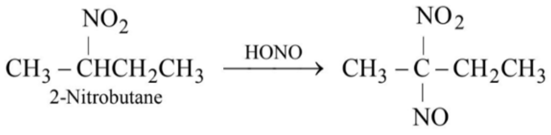
6. **(a,b,d)** Isonitriles (C_6H_5NC) on reduction give 2° amines ($C_6H_5NHCH_3$). All other three methods give aniline.

7. **(a,c,d)** In *p*-$NH_2C_6H_4COOH$, —COOH group is very weak so it can't transfer H^+ to the weakly basic amino group. All other three form zwitterions.

8. **(b,c,d)** In $C_6H_5OCH_3$, —OCH_3 does not sufficiently increase electron density on the ring. Recall that C_6H_5OH undergoes coupling in weakly alkaline medium which converts C_6H_5OH to the more reactive $C_6H_5O^-$. In options (*b*) and (*c*), presence of electron-withdrawing —NO_2 groups increases electrophilic character to such an extent that these diazonium cations can couple even with the compounds having weak electron-releasing groups. Option (d) undergoes coupling reaction easily because –NMe_2 is sufficiently electron-releasing.

9. **(a,b,d)** In *p*-aminophenol all the four positions (2, 3, 5 and 6) can be coupled (positions 2 and 6 in presence of H^+ and positions 3 and 5 in presence of OH^-).

10. **(a,b,d)** *tert*-Nitro compounds (Me_3CNO_2) do not react with HONO because they do not have any α-H. The three others react with HONO as usual.



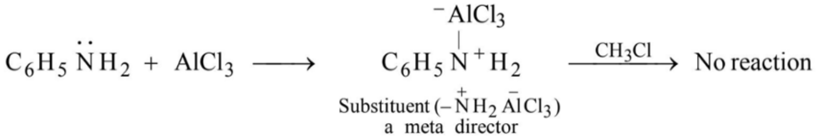
$$CH_3-\underset{}{\overset{NO_2}{\overset{|}{C}}}HCH_2CH_3 \xrightarrow{HONO} CH_3-\underset{\underset{NO}{|}}{\overset{NO_2}{\overset{|}{C}}}-CH_2CH_3$$

2-Nitrobutane

Pseudonitrol (**blue**)

11. **(c,d)** —SO_3H group present in *o*- and *p*-positions are easily replaced.

12. **(a,b,c)**



$$C_6H_5\ddot{N}H_2 + AlCl_3 \longrightarrow C_6H_5\overset{^-AlCl_3}{\overset{|}{N^+}}H_2 \xrightarrow{CH_3Cl} \text{No reaction}$$

Substituent ($-\overset{+}{N}H_2\overset{-}{Al}Cl_3$)
a meta director

However, Friedel-Crafts reactions are the most sluggish electrophilic aromatic substitutions (halogenation occurs most easily), hence if a meta director is present on the ring, the compound does not undergo Friedel-Crafts alkylation/acylation.

E MATRIX-MATCH TYPE

1. **A-p, q; B-r, s; C-r, s; D-s**

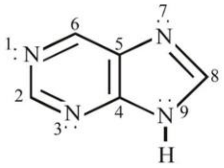
(A) Hydrogen bodning is possible in *ethyl acetoacetate* (due to the presence of enolic group) and in *proteins* (due to the presence of –CO–NH– grouping).

(B) β-Amino acids, like α-amino acids, form *zwitterions* and also undergo *diazotisation* although the diazo salts, so formed, are unstable.

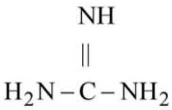
(C) *p*-Amino benzoic acid, like β- and α-amino acids forms *zwitterions* and being 1° aromatic amine also forms, well-known, *diazonium salt*.

(D) Aniline undergoes diazotisation easily.

2. **A-q, r; B-p, s; C-p, r; D-p, r**

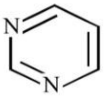


(A)



$$H_2N-\overset{\overset{\large NH}{\|}}{C}-NH_2$$

(B)



(C)

(A) A is aromatic due to 10π electrons, N_1, N_3 and N_7 are sp^2 hybridised their ℓp present in sp^2 orbital are localised hence undergo protonation. The N_9 is also sp^2 hybridised but its ℓp is in *p*-orbital hence involved in delocalisation, and thus not basic.

(B) Due to resonance, all the three nitrogens of guanidine are identical. It is not cyclic, hence non-aromatic.

(C-D) As mentioned above in (A), here the two nitrogens are identical, and the compound is aromatic due to the presence of aromatic sextet.

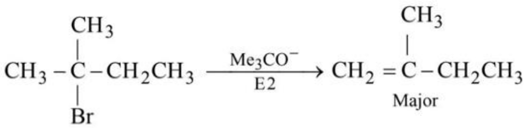
3. **A-r; B-s; C-p, q; D-p, q**

(A) $CHCl_3 \xrightarrow{OH^-} :CCl_2 + HCl$ (α-elimination)

(B) $$CHCl_2-CF_3 \underset{}{\overset{OC_2H_5^-\ \text{fast}}{\rightleftharpoons}} Cl_2\overset{-}{C}-CF_3 \xrightarrow{\text{Slow}} Cl_2C=CF_2$$

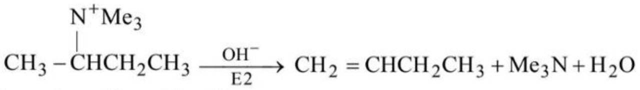
This reaction, although involves two steps; the rate determining step involves only one molecule hence the reaction is labelled as E1. Further, it is the carbanion (conjugate base of $CHCl_2CF_3$) that determines the rate of reaction, hence it is labelled as E1CB.

(C) When the proton to be removed is on the sterically hindered carbon, and the base also has sterically hindered carbon, less substituted alkene is the main product (*Hofmann elimination*)



$$CH_3-\underset{\underset{\large Br}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-CH_2CH_3 \xrightarrow[E2]{Me_3CO^-} \underset{\text{Major}}{CH_2=\overset{\overset{\large CH_3}{|}}{C}-CH_2CH_3}$$

(D) Elimination from quaternary ammonium ions usually gives the least substituted alkene (*Hofmann elimination*).



$$CH_3-\overset{\overset{\large N^+Me_3}{|}}{C}HCH_2CH_3 \xrightarrow[E2]{OH^-} CH_2=CHCH_2CH_3+Me_3N+H_2O$$

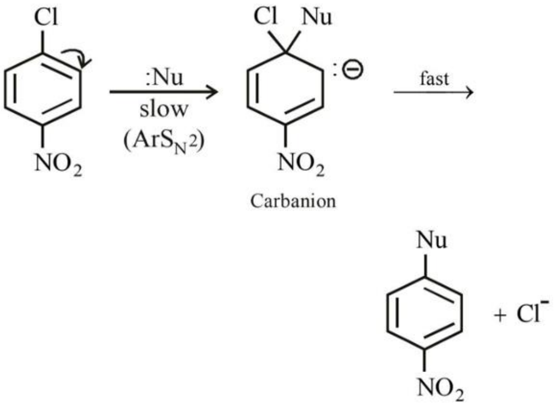
4. **A-p; B-q; C-s; D-r**

. (A) ArS_N1 reactions are rare, and involve carbocation as intermediate. The inportant example is substitution in aromatic diazonium salts.

$$ArN^+\equiv N \xrightarrow{\text{slow}} \underset{\substack{\text{Highly}\\ \text{unstable}}}{Ar^+} + \underset{\text{Highly stable}}{N_2}$$

$$Ar^+ + :Nu \xrightarrow{\text{fast}} Ar-Nu$$

(B)



(C) Higher the bulk of the group present on the nucleophilic centre, lesser is its nucleophilic character.

$${}^-O-H > {}^-O-\underset{\text{bulkyl group}}{C\,(CH_3)_3}$$

(D) Stronger the conjugated acid, weaker will be the base.

$$\underset{\text{stronger acid}}{H_2O} > \underset{\text{weaker acid}}{NH_3}$$

5. **A-q, r; B-q; C-p; D-q, s**

(A) Allylic rearrangements involve the migration of the double bond (and the functional group, if present) from one position to other. These reactions proceed through SN^1, SN^2, SE^1 and SE^2 mechanism; SN^1 involves carbocations (electron-deficient species), while SE^1 involves carbanion.

(B) Hofmann rearrangement involves nitrene $(R-\overset{\overset{\large O}{\|}}{C}-\ddot{N}:)$ intermediate in which nitrogen is electron deficient.

(C) Aldol condensation involves the attack of base on aldehyde or ketone, the reaction will involve the formation of carbanion.

(D) Carbylamine reaction involves the formation of dichlorocarbene ($:CCl_2$) as intermediate which is electron deficient.

✧✧✧