

PLANCESS RANK ACCELERATOR

CHEMISTRY

FOR JEE MAIN & ADVANCED

Amines and Aromatic Compounds Containing Nitrogen

4000+ questions
with topic wise exercises

2000+ problems
of IIT-JEE & AIEEE exams
of last 35 years

4 Levels of
Exercises categorized
into JEE Main & Advanced

7 Types of Questions
based on latest JEE pattern

Detailed Solutions
of all questions are available



PlancEssential

Questions recommended
for revision



**AMINES
AND
AROMATIC
COMPOUNDS
CONTAINING
NITROGEN**

EXERCISE-1 JEE MAIN/BOARDS

Q.1 Arrange the following:

(i) In decreasing order of the pK_b values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength.

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:

(a) Aniline, p-nitroaniline and p-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$,

(iv) In decreasing order of basic strength in gas phase:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:

C_2H_5OH , $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$

Q.2 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

Q.3 Explain Hofmann Bromamide reaction with Mechanism.

Q.4 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis ?

Q.5 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

Q.6 Write one chemical reaction each to illustrate the following

(i) Hofmann Bromamide reaction.

(ii) Gabriel Phthalimide reaction

Q.7 Assign a reason for the following statements

(a) Alkylamines are stronger bases than arylamines.

(b) How would you convert methylamine into ethylamine?

Q.8 Illustrate the following with an example of reaction in each case:

(i) Sandmeyer reaction

(ii) Coupling reaction

Q.9 Write the chemical reaction equations for one example each of the following

(a) A coupling reaction

(b) Hofmann's bromamide reaction

(c) Aryl cyanides cannot be formed by the reaction of aryl halides and sodium cyanide.

Q.10 Account for the following:

(i) Aniline is weaker base than methylamine.

(ii) Aryl cyanides cannot be formed by the reaction of aryl halides and sodium cyanide.

Q.11 Describe tests to distinguish between: Secondary amine and tertiary amine.

Q.12 Account for the following observations:

(i) pK_b for aniline is more than that for methylamine.

(ii) Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.

(iii) Aniline does not undergo Friedel Crafts reaction.

Q.13 State the reactions and reaction conditions for the following conversion

(i) Benzene diazonium chloride to nitrobenzene.

(ii) Aniline to benzene diazonium chloride.

(iii) Ethyl amide to methylamine.

Q.14 Write the physical property of aniline

Q.15 Write the method of formation of benzene diazonium chloride

Q.16 Account for the following:

(i) pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is o- and p- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline.

(v) Aniline does not undergo Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesizing primary amines.

Q.17 How will you convert:

(i) Ethanoic acid into methanamine

- (ii) Hexanenitrile into 1-aminopentane
- (iii) Methanol to ethanoic acid
- (iv) Ethanamine into methanamine
- (v) Ethanoic acid into propanoic acid
- (vi) Methanamine into ethanamine
- (vii) Nitromethane into dimethylamine
- (viii) Propanoic acid into ethanoic acid?

Q.18 Write short notes on the following:

- (i) Carbylamine reaction
- (ii) Diazotisation
- (iii) Hofmann's bromamide reaction
- (iv) Coupling reaction
- (v) Ammonolysis
- (vi) Acetylation
- (vii) Gabriel phthalimide synthesis

Q.19 Accomplish the following conversions

- (i) Nitrobenzene to benzoic acid
- (ii) Benzene to m-bromophenol
- (iii) Benzoic acid to aniline
- (iv) Aniline to 2,4,6-tribromofluorobenzene
- (v) Benzyl chloride to 2-phenylethanamine
- (vi) Chlorobenzene to p-chloroaniline
- (vii) Aniline to p-bromoaniline
- (viii) Benzamide to toluene
- (ix) Aniline to benzyl alcohol.

Q.20 Write the equation of Curtius reaction with mechanism?

Q.21 Complete the following reactions:

- (i) $C_6H_5NH_2 + CHCl_3 + alc. KOH \rightarrow$
- (ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O \rightarrow$
- (iii) $C_6H_5NH_2 + H_2SO_4 (conc.) \rightarrow$
- (iv) $C_6H_5N_2Cl + C_2H_5OH \rightarrow$
- (v) $C_6H_5NH_2 + Br_2(aq) \rightarrow$
- (vi) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow$

Q.22 Give plausible explanation for each of the following:

- (i) Why are amines less acidic than alcohols of comparable molecular masses?
- (ii) Why do primary amines have higher boiling point than tertiary amines?
- (iii) Why are aliphatic amines stronger bases than aromatic amines?

Q.23 Write the reaction and conditions for the following conversions

- (i) Aniline to benzene
- (ii) Methylamine to methyl cyanide
- (iii) Propanenitrile to ethylamine
- (iv) m-Bromoaniline to m-bromophenol
- (v) Nitrobenzene to 2,4,6-tribromoaniline.

Q.24 Write the method of formation of zwitter ion?

Q.25 Explain nitration of aniline?

Q.26 Why aniline does not give Friedel-Crafts reaction?

Q.27 What is Gabriel phthalimide synthesis? For what purpose is it used? Give equation only to explain your answer.

Q.28 Write the equation of carbylamine reaction with mechanism?

Q.29 How will you convert 4-nitrotoluene to 2-bromobenzoic acid?

Q.30 Draw the structure of trimethylamine and tell the shape of the molecule. Show the angle between two methyl groups.

EXERCISE 2 JEE MAIN

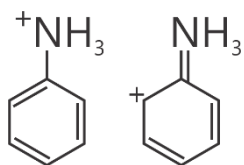
Q.1 When aniline is treated with fuming sulphuric acid at 475K, it gives

- (a) Sulphanilic acid
 (b) Aniline sulphate
 (c) o-aminobenzenesulphonic acid
 (d) m-aminobenzenesulphonic acid

Q.2 When nitrobenzene is treated with Br_2 in presence of FeBr_3 , the major product formed is m-bromonitrobenzene. Statements which are related to obtain m-isomer are:

- (a) The electron-density on meta carbon is more than that on ortho and para positions
 (b) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilized.
 (c) Loss of aromaticity, when Br^+ attacks at the ortho and para positions, and not at meta position.
 (d) Easier loss of H^+ to regain aromaticity from the meta position than from the ortho and para positions.

Q.3 Examine the following two structures for the anilinium ion and choose the correct statement from the ones given below.



- (a) II is not an acceptable canonical structure, because carbonium ions are less stable than ammonium ions
 (b) II is not an acceptable canonical structure, because it is non aromatic
 (c) II is not an acceptable canonical structure, because the nitrogen has 10 valence electrons
 (d) II is an acceptable canonical structure.

Q.4 The correct order of basic strength in CCl_4

- (1) NH_3 (2) RNH_2
 (3) R_2NH (4) R_3N

where R is CH_3 group is

- (a) $3 > 2 > 1 > 4$ (b) $2 > 3 > 4 > 1$
 (c) $3 > 2 > 4 > 1$ (d) None of these

Q.5 Place the following in the decreasing order of basicity.

- (1) Ethylamine (2) 2-aminoethanol

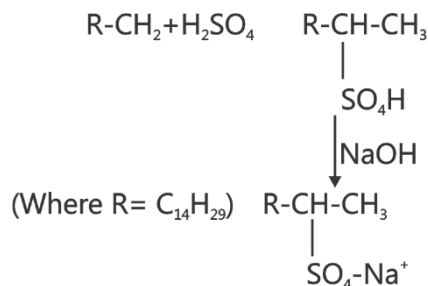
(3) 3-aminopropan-1-ol

- (a) $1 > 3 > 2$ (b) $1 > 2 > 3$
 (c) $2 > 1 > 3$ (d) None of these

Q.6 Which of the following will give a positive carbylamine test?

- (1) H_3CNH_2 (2) $\text{H}_3\text{C-NH-CH}_3$
 (3) $(\text{CH}_3)_3\text{N}$ (4) $\text{C}_6\text{H}_5\text{NH}_2$

Q.7 In the following 2-reaction sequence $\text{R-CH=CH}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{R-CH-CH}_3$ the end product would be useful as

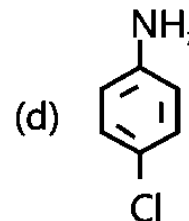
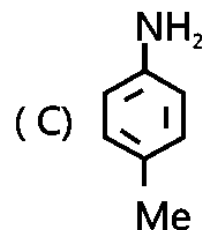
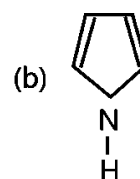
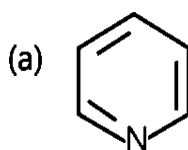


- (a) A fertilizer (b) An explosive
 (c) A detergent (d) None of these

Q.8 The basic strength of amines (ethyl) and ammonia in H_2O is

- (a) $\text{NH}_3 > \text{p} > \text{s} > \text{t}$ (b) $\text{P} > \text{s} > \text{t} > \text{NH}_3$
 (c) $\text{s} > \text{p} > \text{t} > \text{NH}_3$ (d) None of these

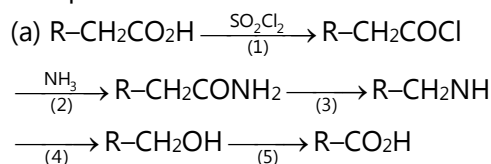
Q.9 Which of the following will have highest K_b value?



Q.10 The product not obtained in the following reaction, $\text{CH}_3\text{-NO}_2 + \text{Cl}_2 + \text{NaOH} \longrightarrow$ is

- (a) ClCH_2NO_2 (b) Cl_2CHNO_2
 (c) Cl_3CNO_2 (d) CH_3NH_2

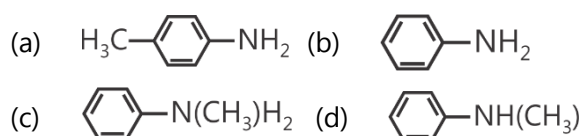
Q.11 A sequential reaction may be performed as represented below:



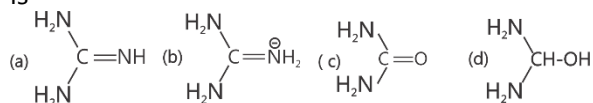
The appropriate reagent for step (3) is

- (a) NaBr (b) Bromine+alkali (c) HBr (d) P₂C₅

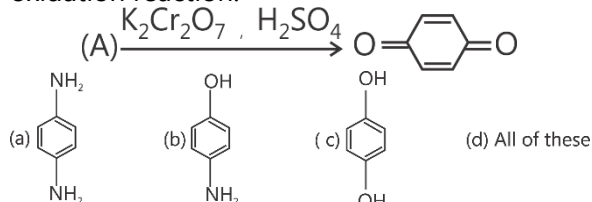
Q.12 Which of the following amine form N-nitroso derivative when treated with NaNO₂ and HCl?



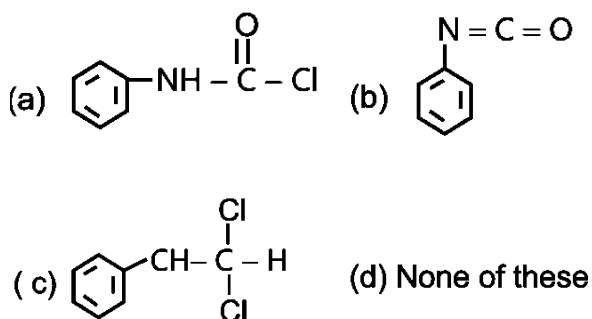
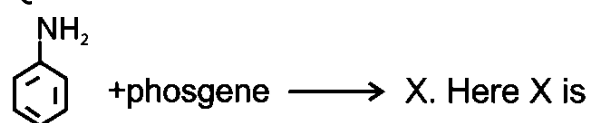
Q.13 The strongest base among the following is



Q.14 Identify compound (A) in the following oxidation reaction.



Q.15



Q.16 Ethylamine undergoes oxidation in the presence of KMnO₄ to give

- (a) CH₃COOH (b) CH₃CH₂OH
 (c) CH₃CHO (d) N-oxide

Q.17 Baker Mulliken's test is used to detect the presence

- (a) -COOH gp (b) -NO₂
 (c) -OH (d) -NH₂

Q.18 t-amines with different alkyl gp has a chiral nitrogen atom still it is optically inactive because

- (a) Chiral N-atoms cannot rotate plane polarized light
 (b) The lone pair prevents the rotation of plane polarized light
 (c) Both of these
 (d) None of these

Q.19 In CH₃NO₂ we can observe

- (a) H-bonding (b) α-halogenation reaction
 (c) Tautomerism (d) all of these

Q.20 Match list I (condition of reaction of nitrobenzene) with list II (products formed) and select the correct answer the codes given below.

- | List-I | List-II |
|-------------------------------|-------------------------|
| (A) Sn and HCl | 1. Hydrazobenzene |
| (B) Zn and NH ₄ Cl | 2. Azoxybenzene |
| (C) Methanolic NaOMe | 3. Phenyl hydroxylamine |
| (D) Zn and KOH | 4. Aniline |
| (a) A-2, B-1, C-3, D-4 | |
| (b) A-4, B-3, C-2, D-1 | |
| (c) A-1, B-4, C-2, D-3 | |
| (d) A-1, B-3, C-2, D-4 | |

Q.21 The increasing order of basicity of RCN, RCN=NR and RHN₂ is

- (a) RCN < RCH=NR < RH₂N
 (b) RNH₂ < RCN < RCH=NR
 (c) CH₃CH₂CONH₂
 (d) CH₃CH(NH₂)COOH

Q.22 How many isomeric amines with that formula C₇H₉N contain a benzene ring?

- (a) two (b) three
 (c) four (d) five

Q.23 Isopropylamine can be obtained by

- (a) (CH₃)₂CHO + NH₂OH $\xrightarrow{\text{LiAlH}_4}$?
 (b) (CH₃)₂CHO + NH₃ $\xrightarrow[\Delta]{\text{H}_2/\text{Ni}}$?
 (c) CHOH + NH₃ \longrightarrow ?
 (d) All of these

Assertion and Reason:

Each of the questions given below consists of two statements, an assertion (A) and reason (R).

Select the number corresponding to the appropriate alternative as follows:

- (a) If both **A** and **R** true and **R** is the correct explanation of **A**, then mark **(a)**
(b) If both **A** and **R** are true but **R** is not the correct explanation of **A**, then mark **(b)**
(c) If **A** is true but **R** is false, then mark **(d)**
(d) If both **A** and **R** false, then mark **(d)**

Q.24 A. Benzyl amine is more basic than aniline.
R. Positive inductive effect of phenyl group creates high electron density around N atom.

Q.25 A. White precipitate of silver chloride gets dissolved in NH_4OH solution.
R. NH_3 reacts with AgCl to form a solution complex with formula $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$.

Q.26 A. o-nitrophenol is more acidic than p-nitrophenol.
R. Nitro group has +M and -I effect.

Q.27 A. 3° amine is proved to be less basic in aq. solution
R. Conjugate acid of 3° amine is poorly solvated in aq. solution.

Q.28 A. In order to convert R-Cl to pure R-NH , Gabriel-phthalimide synthesis can be used.
R. With proper choice for alkyl halides, phthalimide synthesis can be used to prepare 1° , 2° and 3° amines.

Q.29 A. 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.
R. Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

Q.30 A. 1° amides react with $\text{Br}_2 + \text{NaOH}$ to give 1° amines with one carbon atom less than the parent amide.
R. The reaction occurs through intermediate formation of acylnitrene.

Q.31 A. Acetamide reacts with Br_2 in presence of methanoic CH_3ONa to form methyl N-methylcarbonate.

R. Methyl isocyanate is formed as an intermediate which reacts with methanol to form methyl N-methylcarbamate.

PREVIOUS YEARS QUESTIONS JEE MAIN

Q.1 Match the compounds given in **List-I** with their characteristic reactions given in **List-II**. Select the correct option

List-I

1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

2. $\text{CH}_3\text{C}\equiv\text{CH}$

3. $\text{CH}_3\text{CH}_2\text{COOCH}_3$

4. $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

List-II

(i) Alkaline hydrolysis

(ii) With KOH (alcohol) and CHCl_3 produces bad smell

(iii) Gives white ppt. with ammoniacal AgNO_3

(iv) With Lucas reagent cloudiness appears after 5 minutes

(a) 1 (ii), 2 (i), 3 (iv), 4 (iii)

(b) 1 (iii), 2 (ii), 3 (i), 4 (iv)

(c) 1 (ii), 2 (iii), 3 (i), 4 (iv)

(d) 1 (iv), 2 (ii), 3 (iii), 4 (i)

Q.2 A primary amine is formed an amide by the treatment of bromine and alkali. The primary amine has **(BHU 2004)**

(a) 1 carbon atom less than amide

(b) 1 carbon atom more than amide

(c) 1 hydrogen atom less than amide

(d) 1 hydrogen atom more than amide

Q.3 Indicate which nitrogen compound amongst the following would undergo

(a) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}\cdot\text{CH}_3$ (b) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}\cdot\text{NH}_4$

(c) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ (d) $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHOH}$

Hofmann's reaction (i.e. reaction with Br_2 and strong KOH) to furnish the primary amine ($\text{R}-\text{NH}_2$) **(CBSE PMT 1989; Karnataka CET 2006)**

Q.4 The order of basic strength among the following amines in benzene solution is **(AIIMS 1991; RPMT 2002)**

(a) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH}$

(b) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$

(c) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$

(d) $(\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH}$

Q.5 The refluxing of $(\text{CH}_3)_2\text{NCOCH}_3$ with acid gives **(KCET 1996; BHU 2002; BVP 2003)**

(a) $2\text{CH}_3\text{NH}_2 + \text{CH}_3\text{COOH}$

(b) $2\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$

(c) $(\text{CH}_3)_2\text{NH} + \text{CH}_3\text{COOH}$

(d) $(\text{CH}_3)_2\text{NCOOH} + \text{CH}_4$

Q.6 Order of basicity of ethyl amines is **(MP PET/PMT 1988; Kerala PMT 2011)**

(a) Secondary > Primary > Tertiary

(b) Primary > Secondary > Tertiary

(c) Secondary > Tertiary > Primary

(d) Tertiary > Primary > Secondary

Q.7 The following reaction is

$+\text{KOH}(\text{solid}) \xrightarrow{\text{heat}}$

(a) Nucleophilic substitution

(b) Electrophilic substitution

(c) Free radical substitution

(d) None of these

Assertion and Reason:

Read the assertion and reason carefully to mark the correct option out of the options given below:

(a) If both assertion and reason are true and the reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.

(c) If assertion is true but reason is false.

(d) If assertion is false but reason is true.

Q.8 Assertion: Benzene diazonium chloride does not give tests for nitrogen.

Reason: N_2 gas lost during heating **(AIIMS 1999)**

Q.9 Assertion: Amines are basic in nature.

Reason: Presence of lone pair of electron on nitrogen atom. **(AIIMS 1999)**

Q.10 Assertion: Alkyl isocyanides in acidified water give alkyl formamides.

Reason: In isocyanides, carbon first acts as a nucleophile then as an electrophile. **(AIIMS 2005)**

Q.11 Assertion: Amines are more basic than esters and ethers.

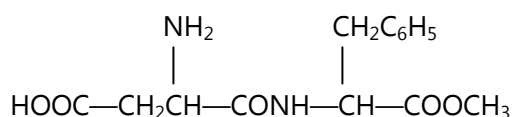
Reason: Nitrogen is less electronegative than oxygen. It is in better position to accommodate the positive charge on the proton. **(AIIMS 2007)**

Q.12 Assertion: Nitrobenzene is used as a solvent in Friedel-Craft's reaction.

Reason: Fusion of nitrobenzene with solid KOH gives a low yield of a mixture of o- and p- nitro phenols. **(AIIMS 2008)**

EXERCISE 1 JEE ADVANCED

Q.1 Aspartame, an artificial sweetener, is a peptide and has the following structures:



- Identify the four functional groups.
- Write the zwitter ionic structure
- Write the structures of the amino acids obtained from the hydrolysis of aspartame.
- Which of the two amino acids is more hydrophobic?

Q.2 Compound of A (molecular formula $\text{C}_9\text{H}_{11}\text{NO}$) gives a positive Tollen's test and is soluble in dilute HCl. It gives no reaction with benzene sulphonyl chloride or with NaNO_2 and HCl at 0°C . (A), upon oxidation with KMnO_4 gives an acid (B). When (B) is heated with soda-lime, compound (C) is formed which reacts with NaNO_2 and HCl at $0-5^\circ\text{C}$. What is (A)?

Q.3 An organic compound A, when treated with nitrous acid yields an alcohol B, $\text{C}_4\text{H}_{10}\text{O}$ with the evolution of N_2 . B on careful oxidation yields a substance C of vapour density 36 which forms oxime; B can react with NaHSO_3 but does not reduce Fehling solution. Identify compound A and write the structural formulae of the isomeric compounds that behave with HNO_2 in the same manner.

Q.4 An organic compound (A), $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$, is insoluble in both dilute acid and base and its dipole moment is zero. Deduce the structure of (A).

Q.5 Explain the following observations:

- Aniline dissolves in aqueous HCl.
- The amino group in ethylamine is basic whereas that in acetamide it is not basic.
- Dimethylamine is a stronger base than trimethylamine.
- Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acids.

Q.6 Explain, why?

(1) Glycine exists as $\text{H}_3\text{N}^+\text{CH}_2\text{COO}^-$ while anthranilic acid, $p\text{-NH}_2\text{C}_6\text{H}_4\text{COOH}$ does not exist as dipolar ion.

(2) Benzenesulphonic acid is a stronger acid than benzoic acid.

(3) A weakly basic solution favours coupling with phenol.

(4) It is difficult to prepare pure amines by ammonolysis of alkyl halides.

Q.7 Explain with reason?

(1) Although trimethylamine and n-propylamine have same molecular weight, the former boils at a lower temperature (3°C) than the latter (49°C).

(2) Dimethylamine is a stronger base than methylamine but trimethylamine is a weaker base than both dimethylamine and methylamine.

(3) Although trimethylamine and n-propylamine have same molecular weight, the former boils at a lower temperature (3°C) than the latter (49°C). Explain.

(4) Silver chloride dissolves in aqueous solution of methylamine. Explain.

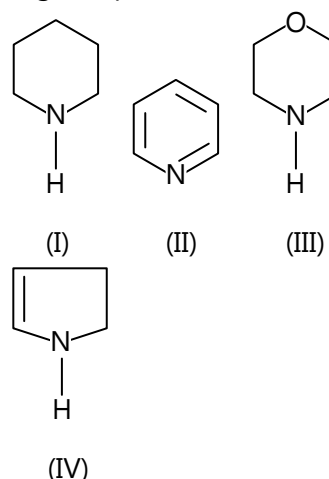
Q.8 Explain it?

(1) An aqueous solution of ethylamine gives a red precipitate with ferric chloride. Explain.

(2) Tertiary amines do not undergo acetylation. Comment

(3) 2,6-Dimethyl-N,N-dimethylaniline, although has a free p-position, does not undergo coupling with benzene diazonium chloride. Comment.

(4) In the following compounds:



The order of basicity is I > III > II > IV. Explain.

Q.9 Explain it with reason.

(1) tert-Butylamine cannot be prepared by the action of NH_3 on tert-butyl bromide.

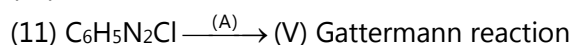
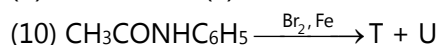
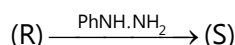
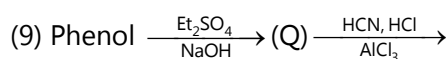
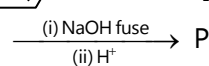
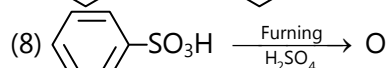
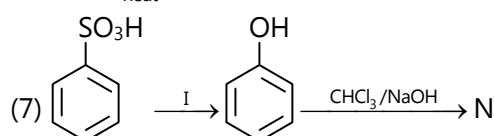
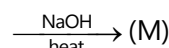
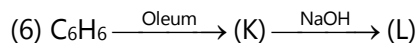
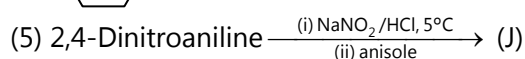
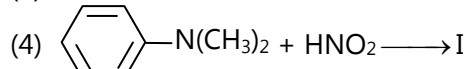
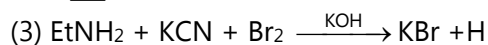
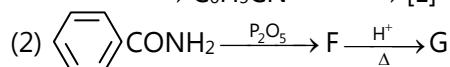
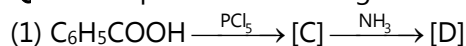
(2) Isocyanides are hydrolysed by dilute acids but not by alkalis to form amine and formic acid.

(3) How will you explain the acidic nature of 1° and 2° nitroalkanes?

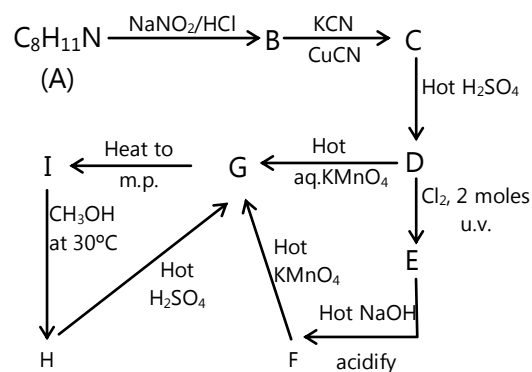
(4) Aniline does not undergo Friedel Craft's reaction?

(5) Although boron trifluoride adds on trimethylamine, it does not add on triphenylamine. Comment.

Q.10 Complete the following reactions:



Q.11 Give structures for the compounds (A) to (I):



Q.12 When 2.25 g of an unknown amine was treated with nitrous acid, the evolved nitrogen, corrected to S.T.P. measured 560 ml. The alcohol isolated from the reaction mixture gave a positive iodoform reaction. What is the structural formula of the unknown amine?

Q.13 The aqueous solution of a nitrogen and chlorine containing organic compound (A) is acidic towards litmus. (A) on treatment with aqueous NaOH gives a compound (B), containing, but not chlorine. Compound (B) on treatment with $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ in the presence of NaOH gives an insoluble product (C), $\text{C}_{13}\text{H}_{13}\text{NO}_2\text{S}$. Give the structures of compounds (A) and (B).

Q.14 An organic compound (A) composed of C, H and O gives characteristic colour with ceric ammonium nitrate. Treatment of (A) with PCl_5 gives (B), which reacts with KCN to form (C). The reduction of (C) with warm $\text{Na}/\text{C}_2\text{H}_5\text{OH}$ products (D), which on heating gives (E) with evolution of ammonia. Pyridine is obtained on treatment of (E) with nitrobenzene. Give structure of compounds (A) to (E) with proper reasoning.

Q.15 One mole of bromo derivative (A) and mole of NH_3 react to give one mole of an organic compound (B). (B) reacts with CH_3I to give (C). Both (B) and (C) react with HNO_2 to give compounds, (D) and (E) respectively. (D) on oxidation and subsequent decarboxylation gives 2-methoxy-2-methyl propane. Give structures of compounds (A) to (E) with proper reasoning.

Q.16 What happens with cyclopentanone reacts with

(a) $\text{CH}_3\text{CH}_2\text{NH}_2$ (1° amine)

(b) $(\text{CH}_3\text{CH}_2)_2\text{NH}$ (2° amine)

Q.17 Cyclohexyl amine is a stronger base than aniline. Why?

Q.18 How does the formation of 2° and 3° amines can be avoided during the preparation of 1° amines by alkylation?

Q.19 It is necessary to acetylate aniline first for preparing bromoaniline. Why?

Q.20 Dimethyl amine is a stronger base than methylamine but trimethylamine is a weaker base than both dimethyl amine and methylamine. Why?

Q.21 From analysis and molecular weight determination, the molecular formula of (A) is $\text{C}_3\text{H}_7\text{NO}$. The compound gave following reactions.

(i) On hydrolysis, it gives an amine (B) and a carboxylic acid (C)

(ii) Amine (B) reacts with benzene sulphonyl chloride and gives a product which is insoluble in aqueous sodium hydroxide solution.

(iii) Acid (C) on reaction with Tollen's reagent gives a silver mirror when are A, B and C. Explain the reactions.

Q.22 An optically active amine (A) is subjected to exhaustive methylation and Hofmann elimination to yield an alkene (B). (B) on ozonolysis gives an equimolar mixture of formaldehyde and butanal. Deduce the structures of (A) and (B). Is there any structural isomer to (A), if yes draw its structure.

Q.23 An aromatic compound (a) having molecular formula $\text{C}_7\text{H}_7\text{NO}_2$ dissolves in NaHCO_3 to evolve CO_2 and when reacted with NaNO_2/HCl forms (b), $\text{C}_7\text{H}_6\text{O}_3$. (B) dissolves in NaHCO_3 and gives colour reaction with FeCl_3 and can be prepared by the action of CCl_4 and NaOH on phenol. When (B) is reacted with excess HNO_3 , it forms (C), $\text{C}_6\text{H}_3\text{N}_3\text{O}_7$. (C) undergoes acetylation and decomposes NaHCO_3 to evolve CO_2 . On reaction with PCl_5 (C) is converted to (D), $\text{C}_6\text{H}_5\text{N}_3\text{O}_6\text{Cl}$ which when reacted with water gives back (C). Identify compounds (A) to (D).

Q.24 Compound (A) having M.F. $\text{C}_8\text{H}_8\text{O}$ on treatment with $\text{NH}_2\text{OH}.\text{HCl}$ gives (B) and (C). (B) and (C) rearrange to give (D) and (E), respectively on treatment with acid. Compounds (B), (C), (D) and (E) are all isomers of molecular formula $\text{C}_8\text{H}_9\text{NO}$. When (D) is boiled with alcoholic KOH , and oil (F) $\text{C}_6\text{H}_7\text{N}$ separated out. (F) reacts rapidly with CH_3COCl to give back (D). On the other hand (E) on boiling with alkali followed by acidification gives a white solid (G), $\text{C}_7\text{H}_6\text{O}_2$. Identify the compounds (A) to (G).

Q.25 An aromatic compound (A), having M.F. $\text{C}_7\text{H}_5\text{NO}_2\text{Cl}_2$ on reduction with Sn/HCl gives (B), which on reaction with NaNO_2/HCl gives (C). Compound (B) is unable to form a dye with β -naphthol. However, (C) gives red colour with ceric ammonium nitrate and on oxidation gives an acid (D), having equivalent weight 191. Decarboxylation of (D) gives (e) which forms a single mononitro derivative (F), on nitration. Give the structures of (A) to (F) with proper reasoning.

Q.26 An organic compound (A) of molecular weight 135, on boiling with NaOH evolves a gas which gives white dense fumes on bringing a rod dipped in HCl near it. The alkaline solution thus obtained on acidification gives the precipitate of a compound (B) having molecular weight 136. Treatment of (A) with HNO_2 also yields (B), whereas its treatment with Br_2/KOH gives (C). Compound (C) reacts with cold HNO_2 to gives (D), which give red colour with ceric ammonium nitrate. On the other hand, (E) an isomer of (A) on boiling with dilute HCl gives an acid(F), having molecular weight 136. On oxidation followed by heating, (F) gives an anhydride (G), which condenses with benzene in the presence of anhydrous AlCl_3 to give anthraquinone. Give the structures of (A) to (G) with proper reasoning.

Q.27 An organic compound (A) having M.F. $\text{C}_7\text{H}_9\text{N}$ on treatment with NaNO_2 and HCl at room temperature forms another compound (B), $\text{C}_7\text{H}_8\text{O}$. When (A) or (B) is treated with bromine water, they form dibromo derivatives, When (A) is reacted with chloroform and alkali,

it forms (C) having the molecular formula $C_8H_{17}N$. Hydrolysis of (C) followed by reaction with $NaNO_2$ and HCl at low temperature and subsequent reaction with HCN in the presence of Cu (D), which is isomeric to (C). (D) on hydrolysis followed by oxidation gives a dibasic acid which on halogenation forms only one monohaloderivative. Identify the compounds (A) to (E).

Q.28 An optically active compound (A), $C_3H_7O_2N$ forms a hydrochloride but dissolves in water to give a neutral solution. On heating with soda lime (A) yields (B) C_2H_7N . Both (A) react with $NaNO_2$ and HCl the former yielding a compound (C) C_3H_6O , which on heating is converted to (D), $C_6H_8O_4$ while the latter yields (E), C_2H_6O . Account for the above reactions and suggest how (A) may be synthesized.

Q.29 An optically inactive acid (A), $C_5H_8O_5$, on being heated lost CO_2 to give an acid (B), $C_4H_8O_3$ capable of being resolved. On action of sulphuric acid, B gave an acid C whose ethyl ester gave (D) on the action of hydrogen and platinum. (D) with conc. NH_3 gave E, C_4H_9OH which with Br_2 and KOH solution gave (F), C_3H_9N . F with HNO_2 gave G (G) on mild oxidation gave H. Both A and H gave the iodoform reaction. Elucidate the reaction mechanism and suggest a synthesis of (C).

Q.30 A neutral compound (A) C_8H_9OH on treatment with $NaOBr$ forms an acid soluble substance C_7H_9N . On addition of aqueous $NaNO_2$ to a solution of B in dilute HCl at $0-5^\circ C$, an ionic compound (C) $C_7H_7N_2Cl$ is obtained. (C) yields a red dye with alkaline β -naphthol solution. When treated with potassium cuprocyanide (C) yields a neutral substance (D) C_8H_7N . ON hydrolysis (D) gives E ($C_8H_6O_4$). (F) on nitration yields two isomeric mononitro derivatives (G and H) having molecular formula $C_8H_5NO_6$. Write the reactions involved in different steps.

EXERCISE 2 JEE ADVANCED

Q.1 Match the compounds in list I with the appropriate test that will be answered by each one of them in list II from the combinations shown.

Selects the correct answer using the codes given below the list.

List-I

- (A) Propyne
 (B) Ethyl benzoate
 (C) Acetaldehyde
 (D) Aniline

List-II

- 1.Reduces Fehling's solution
 2.Forms a precipitate with $\text{AgNO}_3 + \text{C}_2\text{H}_5\text{OH}$
 3.Insoluble in water, but dissolves in aqueous NaOH upon heating
 4.Dissolves in dil. HCl in the cold and is reprecipitated by the addition of alkali

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

Q.2 Activation of benzene ring by $-\text{NH}_2$ in aniline can be reduced by treating with

- (a) Dilute HCl (b) Ethyl alcohol
 (c) Acetic acid (d) Acetyl chloride

Q.3 Dipolar ion structure for amino acid is

- (a) $\text{H}_2\text{N}-\underset{\text{R}}{\text{CH}}-\text{COOH}$ (b) $\text{H}_3\text{N}^+-\underset{\text{R}}{\text{CH}}-\text{COO}^-$
 (c) $\text{H}_3\text{N}^+-\underset{\text{R}}{\text{CH}}-\text{COO}^-$ (d) None of these

Q.4 $-\text{NH}_2$ group shows acidic nature while reacts with reagent.

- (a) Na (b) CS_2
 (c) $\text{Br}_2 + \text{NaOH}$ (d) Water

Q.5 Which of the following does not give ethylamine on reduction

- (a) methyl cyanide (b) Ethyl nitrile
 (c) Nitro ethane (d) Acetamide

Q.6 Aniline is a weaker base than ethyl amine because

- (a) Phenyl gp in aniline is a +R gp
 (b) Ethyl gp in ethyl amine decreases the electron density on nitrogen atom

(c) The lone pair of electron on nitrogen atom in aniline is delocalized over aniline.

(d) Aniline is less soluble in water than ethylamine

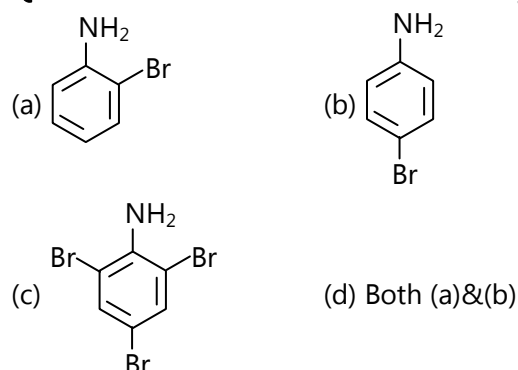
Q.7 Diazonium coupling reaction with aniline should be carried out in

- (a) Weakly basic medium
 (b) Weakly acidic medium
 (c) Strongly basic medium
 (d) Strongly acidic medium

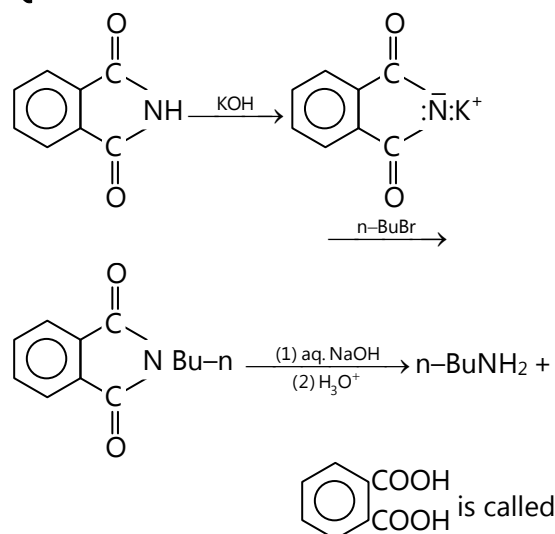
Q.8 For CH_3CHO , CH_3NO_2 , CH_3COOH

- (a) All have same chemical property
 (b) All have one common chemical behaviour
 (c) All are basic
 (d) None of these

Q.9 Bromine in CS_2 reacts with aniline to give



Q.10 The reaction:



- (a) Carbylamine reaction
 (b) Hofmann reaction
 (c) Gabriel phthalimide synthesis
 (d) Cope reaction

Q.11 The conjugate acid of $\text{HO}(\text{CH}_2)_3\text{NH}_2$ is

- (a) $\text{H}_2\text{O}^+(\text{CH}_2)_3\text{NH}_2$ (b) $\text{HO}(\text{CH}_2)_3\text{NH}_3^+$
 (c) $\text{O}^-(\text{CH}_2)_3\text{NH}_2$ (d) $\text{HO}(\text{CH}_2)_3\text{NH}^+$

Q.12 Consider the following compounds:

- $\text{H}_2\text{C}=\text{CHCH}_2\text{NH}_2$
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
- $\text{HC}\equiv\text{CCH}_2\text{NH}_2$

The increasing order of basicity is

- (a) $3 < 1 < 2$ (b) $3 < 2 < 1$
 (c) $2 < 1 < 3$ (d) None of these

Q.13 Reaction of RCONH_2 with a mixture of Br_2 and KOH gives RNH_2 as the main product. The intermediate involved in the reaction is

- (a) $\begin{array}{c} \text{Br}-\text{O}-\text{NHBr} \\ || \\ \text{C} \end{array}$ (b) $\text{R}-\text{NHBr}$
 (c) $\begin{array}{c} \text{O} \\ || \\ \text{R}-\text{C}-\text{N} \begin{array}{l} \nearrow \text{Br} \\ \searrow \text{Br} \end{array} \end{array}$ (d) $\text{R}-\text{C}=\text{N}=\text{O}$

Q.14 Amines are highly soluble in:

- (a) Alcohol (b) Diethyl ether
 (c) benzene (d) Water

Q.15 Which of the following reagents can convert benzene diazonium chloride into benzene?

- (a) Water
 (b) Acid
 (c) Hypophosphorous acid
 (d) HCl

Q.16 The bromination of aniline produces

- (a) 2-bromoaniline
 (b) 4-bromoaniline
 (c) 2,4,6-tribromoaniline
 (d) 2,6-dibromoaniline

Q.17 The compound, which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is

- (a) Methyl amine (b) Ethylamine
 (c) Diethylamine (d) Triethylamine

Q.18 Carbylamine test is performed in alcoholic KOH by heating a mixture of

- (a) Chloroform and silver powder
 (b) Trihalogenated methane and a primary amine
 (c) An alkyl halide and a primary amine

(d) An alkyl cyanide and a primary amine.

Comprehension:

Arene diazonium salts are more stable than alkanediazonium salts due to dispersal of the positive charge on the benzene ring. Obviously electron donating groups favour diazotisation by retarding the decomposition of diazonium salts to phenyl cation. The high reactivity of arenediazonium salts is due to the excellent leaving ability of the diazo group as N_2 gas. Therefore, diazonium salts undergo a number of substitution reactions in which the diazo group is replaced by a monovalent atom/group such as H (by H_3PO_2 in presence of Cu^+ ions, $\text{CH}_3\text{CH}_2\text{OH}$, NaBH_4 etc), OH (by boiling in presence of mineral acids), OCH_3 (by heating with CH_3OH) Cl (by CuCl/HCl or Cu/HCl), Br (by CuBr/HBr or Cu/HBr) I (by KI in presence of Cu^+ ions), F (by first converting into N_2F_4 followed by heating), CN (by first neutralizing with Na_2CO_3 and then reacting with KCN/CuCN), NO_2 (by first neutralizing with Na_2CO_3 and then treating with NaNO_2) phenyl or substituted phenyl (by treating with benzene or substituted benzene in presence of NaOH) etc. Diazonium salts also couple with phenols and aromatic amines to form coloured azo dyes. The reactivity of diazonium salts towards coupling reactions is favoured by presence of electron withdrawing groups; the reactivity of 2,4,6-trinitrobenzenediazonium chloride is so high that it even couples with reactive hydrocarbons such as mesitylene.

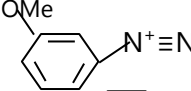

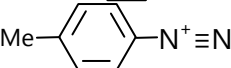
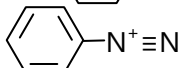
Q.19 Consider the following ions:

- (a) $\text{Me}_2\text{N}-\text{C}_6\text{H}_4-\text{N}^+\equiv\text{N}$
 (b) $\text{O}_2\text{N}-\text{C}_6\text{H}_3(\text{NO}_2)_2-\text{N}^+\equiv\text{N}$
 (c) $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{N}^+\equiv\text{N}$
 (d) $\text{CH}_3-\text{C}_6\text{H}_4-\text{N}^+\equiv\text{N}$

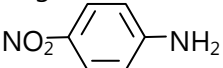
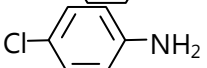
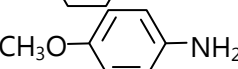
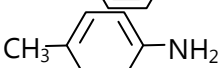
The reactivity of these ions towards azo coupling reactions under similar conditions is

- (a) $\text{I} < \text{IV} < \text{II} < \text{III}$ (b) $\text{I} < \text{III} < \text{IV} < \text{II}$
 (c) $\text{III} < \text{I} < \text{II} < \text{IV}$ (d) $\text{III} < \text{I} < \text{IV} < \text{II}$

Q.20 Which of the following diazonium salts when boiled with dil. H_2SO_4 gives the corresponding phenol most readily?

- (a) 
- (b) 
- (c) 
- (d) 

Q.21 Which of the following arylamines undergoes diazotisation most readily?

- (a) 
- (b) 
- (c) 
- (d) 

Q.22 The product formed when bromobenzene reacts with benzenediazonium chloride in presence of NaOH is

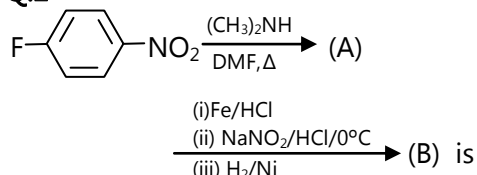
- (a) Diphenyl
(b) p-Bromodiphenyl
(c) p,p'-Dibromodiphenyl
(d) p-Bromoazobenzene

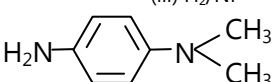
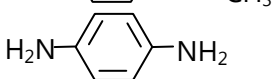
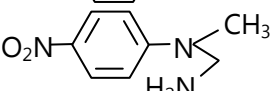
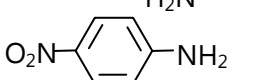
PREVIOUS YEARS QUESTIONS JEE ADVANCED

Q.1 Benzene diazonium chloride on reaction with phenol in weakly basic medium gives (1998)

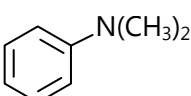
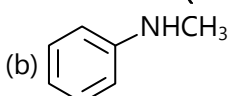
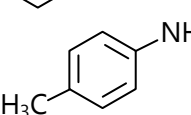
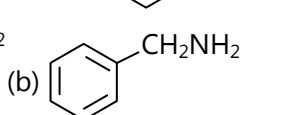
- (a) diphenyl ether
 (b) p-hydroxy azobenzene
 (c) chlorobenzene
 (d) benzene

Q.2



- (a) 
 (b) 
 (c) 
 (d) 

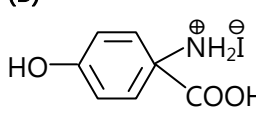
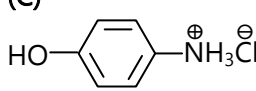
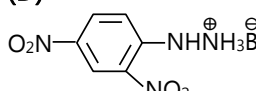
Q.3 Amongst the compounds given, the one that would form a brilliant coloured dye on treatment with NaNO_2 in dil. HCl followed by addition to an alkaline solution of β -naphthol is (2011)

- (a)  (b) 
 (c)  (b) 

Q.4 Match the columns

Match the compounds in Column I with their characteristic test(s)/reaction(s) given in Column II.

Column I	Column II
(A) $\text{H}_2\text{N}-\text{NH}_3^+\text{Cl}^-$	(P) Sodium fusion extract of the compound gives Prussian blue colour with FeSO_4

(B) 	(Q) Gives positive FeCl_3 test
(C) 	(R) Gives white precipitate with AgNO_3
(D) 	(S) Reacts with aldehydes to form the corresponding hydrazone derivative.

Fill in the Blanks

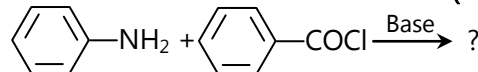
Q.5 In an acidic medium,behaves as the strongest base. (nitrobenzene, aniline, phenol) (1981)

Q.6 The high melting point and insolubility in organic solvents of sulphanilic acid are due to itsstructure. (1994)

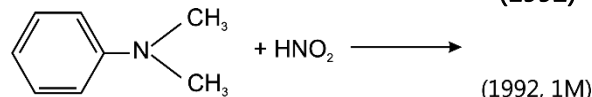
Q.7 State the equation for the preparation of following compound. Chlorobenzene from aniline (in two steps) (1982)

Q.8 State the conditions under which the following preparation carried out. "Aniline from benzene" (1983)

Q.9 Complete the following with appropriate structures: (1986)



Q.10 Write the structure of the major organic product expected from the following reaction. (1992)



• PlancEssential Questions •

RECOMMENDED DURING REVISION

EXERCISE 1 JEE MAIN/BOARDS

Q.1 (iii) Q.3 Q.12 (iii) Q.17 (ii,vi) Q.19(iv) Q.22(ii) Q.27

EXERCISE 2 JEE MAIN

Q.2 Q.11 Q.15 Q.20 Q.28

PREVIOUS YEARS' JEE MAIN

Q.1 Q.5 Q.10

EXERCISE 1 JEE ADVANCED

Q.2 Q.6 (4) Q.7 (4) Q.14 Q.23 Q.29

EXERCISE 2 JEE ADVANCED

Q.8 Q.19 Q.21

PREVIOUS YEARS' JEE ADVANCED

Q.2 Q.4

ANSWER KEY

EXERCISE 2 JEE MAIN

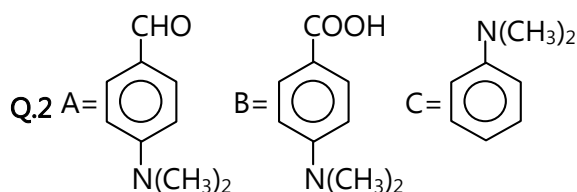
Q.1 a	Q.9 a	Q.17 b	Q.25 a
Q.2 a, b	Q.10 d	Q.18 d	Q.26 d
Q.3 c	Q.11 b	Q.19 d	Q.27 a
Q.4 d	Q.12 d	Q.20 b	Q.28 c
Q.5 b	Q.13 a	Q.21 a	Q.29 b
Q.6 d	Q.14 d	Q.22 b	Q.30 a
Q.7 c	Q.15 b	Q.23 a	Q.31 a
Q.8 d	Q.16 d	Q.24 c	

PREVIOUS YEARS QUESTIONS JEE MAIN

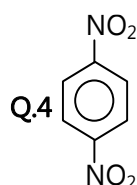
Q.1 c	Q.5 b	Q.9 a
Q.2 a	Q.6 c	Q.10 a
Q.3 c	Q.7 a	Q.11 a
Q.4 b	Q.8 a	Q.12 b

EXERCISE-1 JEE ADVANCED

Q.1 The hydrolysed products are aspartic acid and phenylalanine.



Q.3 $\text{CH}_3-\underset{\text{NH}_2}{\text{CH}}-\text{C}_2\text{H}_5$, The other isomers should be p-amines only



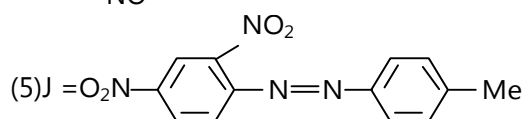
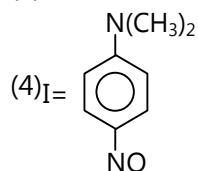
Q.10

(1) C = $\text{C}_6\text{H}_5\text{COCl}$; D = $\text{C}_6\text{H}_5\text{CONH}_2$

E = $\text{C}_6\text{H}_5\text{CHNH}_2$

(2) F = $\text{C}_6\text{H}_5\text{CN}$; G = $\text{C}_6\text{H}_5\text{COOH}$

(3) H = EtNHBr

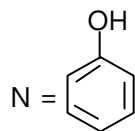


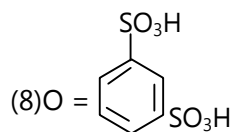
(6) K = $\text{C}_6\text{H}_5\text{SO}_3\text{H}$

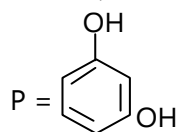
L = $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$

M = $\text{C}_6\text{H}_5\text{OH}$

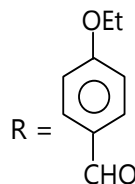
(7) I = NaOH

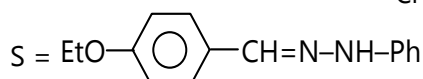


(8) O = 



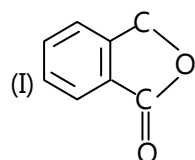
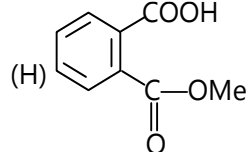
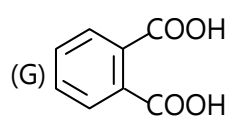
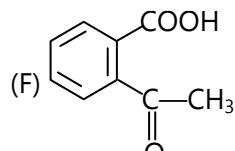
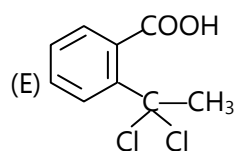
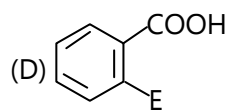
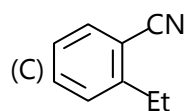
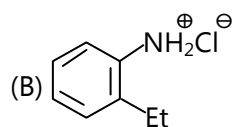
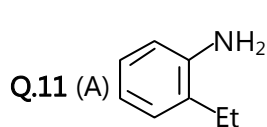
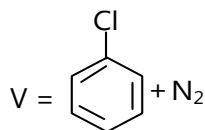
(9) Q = Ph-O-Et



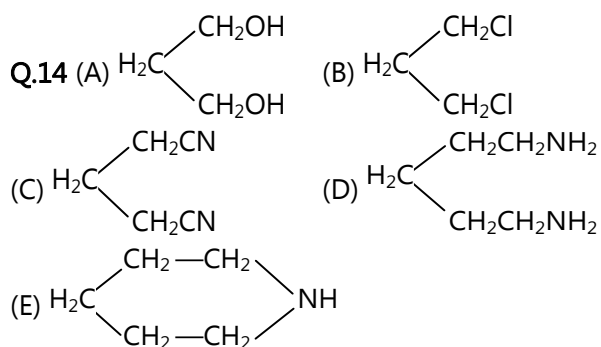
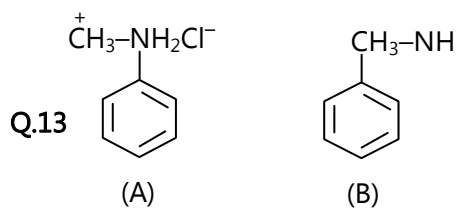
S = 

(10) T =  + para isomer

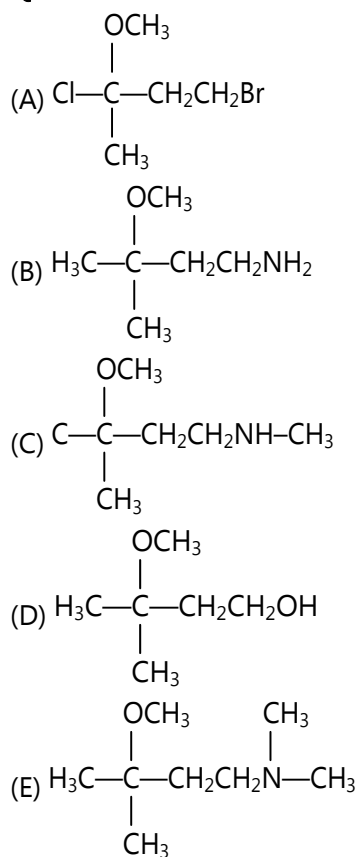
(11) U = Cu Powder



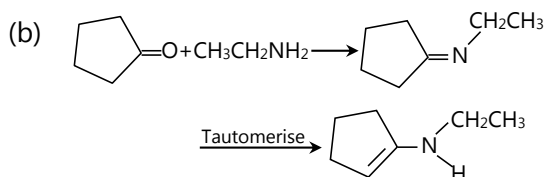
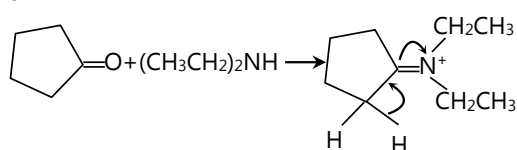
Q.12 C₂H₅NH₂



Q.15



Q.16 (a)



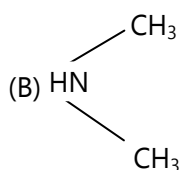
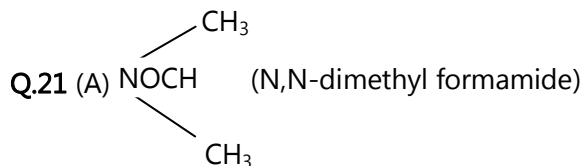
Q.17 Aniline is a weak base than cyclohexylamine because of resonance.

Amines and Aromatic Compounds Containing Nitrogen

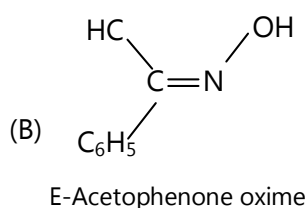
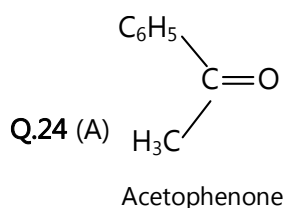
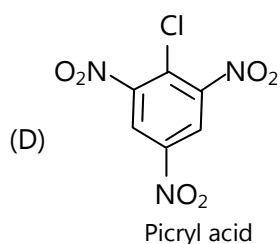
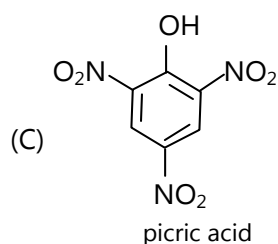
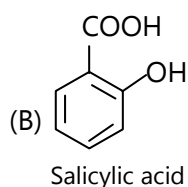
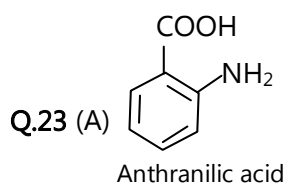
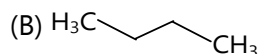
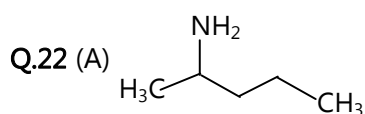
Q.18 Use of excess ammonia reduces chances of reaction of 1° amine with alkyl halide to form 2° and 3° amines.

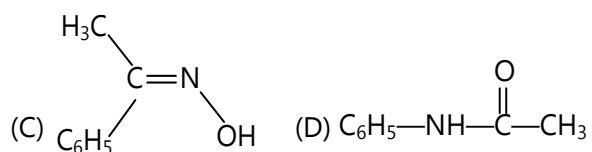
Q.19 Amino group, being activating group, activates bromination of aniline and forms tribromoaniline.

Q.20 Dimethyl amine is stronger base because of inductive effect. Trimethyl amine is a weaker base because positive charge on nitrogen could be stabilized and due to crowding by alkyl groups around the nitrogen atom protonation cannot take place.



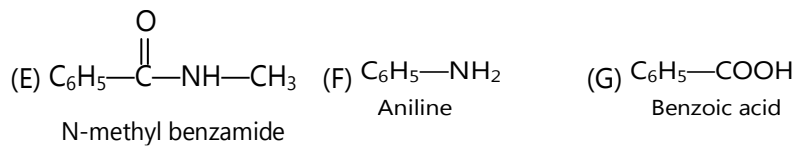
(C) HCOOH





Z-Acetophenone oxime

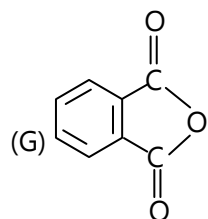
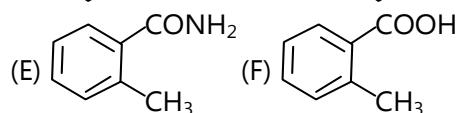
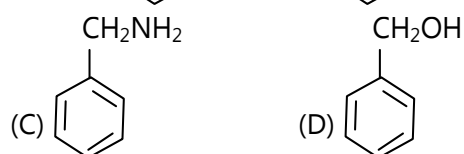
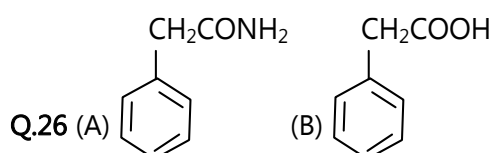
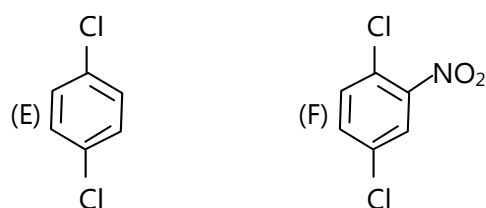
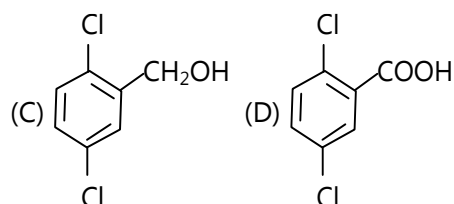
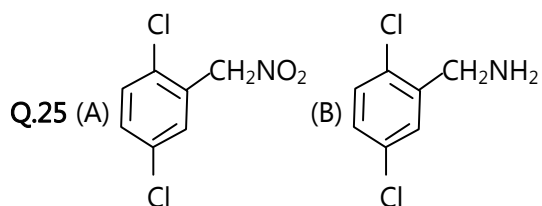
Acetanilide

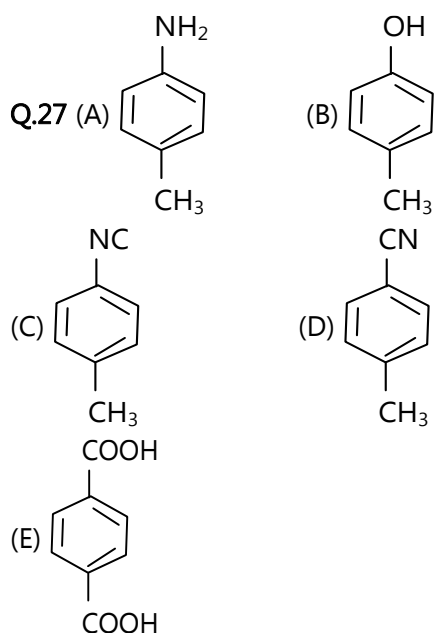


N-methyl benzamide

Aniline

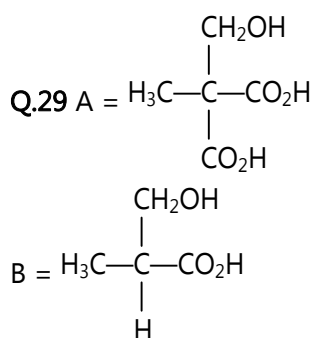
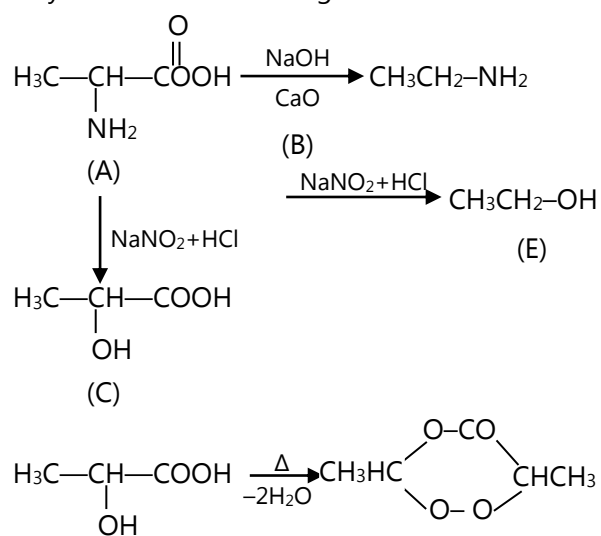
Benzoic acid

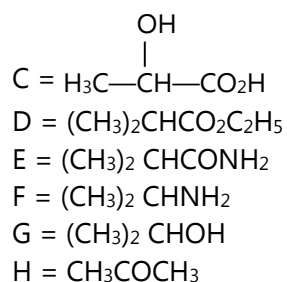




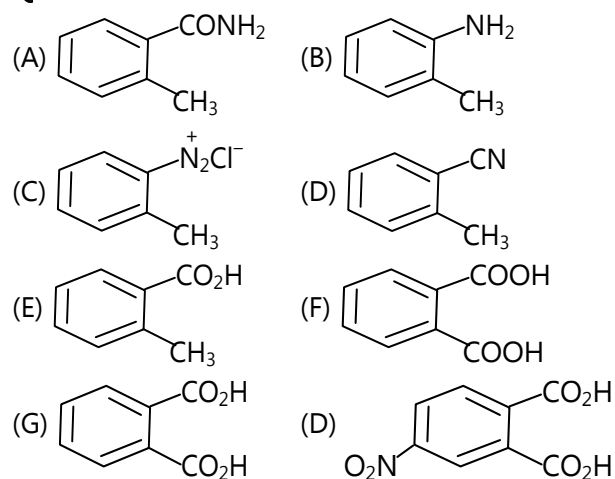
Q.28 Degree of unsaturation of A = 2

Since A forms hydrochloride and dissolves in water to give a neutral solution, it contains both a basic and an acidic functional group. It is likely to be amino acid as the molecular formula contains one N and 2 O-atoms. On decarboxylation it forms an amine B. Degree of unsaturation of B = 0. Therefore, B is a saturated amine. B reacts with NaNO_2 and dilute HCl forming (E) $\text{C}_2\text{H}_5\text{OH}$. Thus, B is $\text{CH}_3\text{CH}_2\text{-NH}_2$. A also reacts with NaNO_2 and dilute HCl forming C, a hydroxyl acid, which forms a cyclic diester on heating. All the reactions can be given as





Q.30



EXERCISE 2 JEE ADVANCED

Q.1 b
 Q.2 d
 Q.3 c
 Q.4 c
 Q.5 b
 Q.6 c

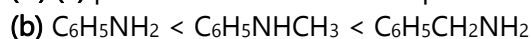
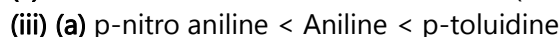
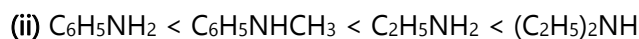
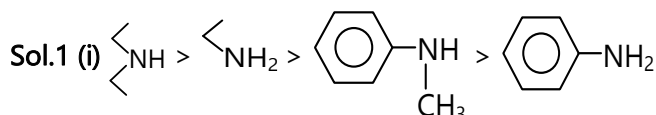
Q.7 b
 Q.8 b
 Q.9 c
 Q.10 c
 Q.11 b
 Q.12 a

Q.13 a
 Q.14 d
 Q.15 c
 Q.16 c
 Q.17 c
 Q.18 b

Q.19 b
 Q.20 a
 Q.21 c
 Q.22 b

SOLUTIONS

EXERCISE – I JEE MAIN

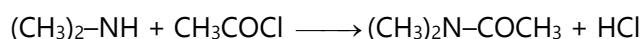
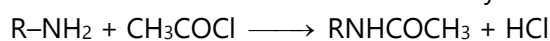


(iv) Refer Theory

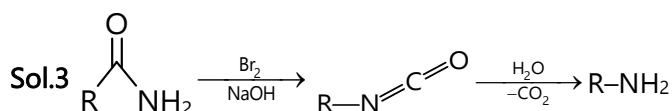
(v) Refer Theory

(vi) Refer Theory

Sol.2 1° and 2° amines react with acetyl chloride to form acetyl derivatives.



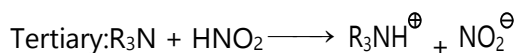
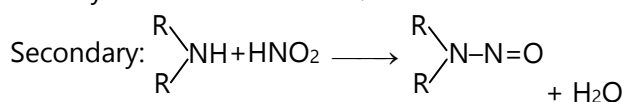
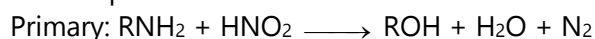
Tertiary amine do not undergo this reaction.



Reaction of a primary amide to form primary amine with one fewer carbon atom.

Sol.4 +ve charge or secondary carbon is not stable

Sol.5 Aliphatic amines

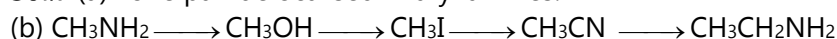


Aromatic Amines forms diazonium ions.

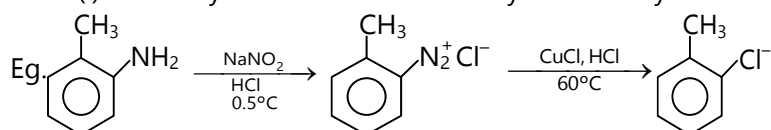
Sol.6 (i) Refer Sol.2

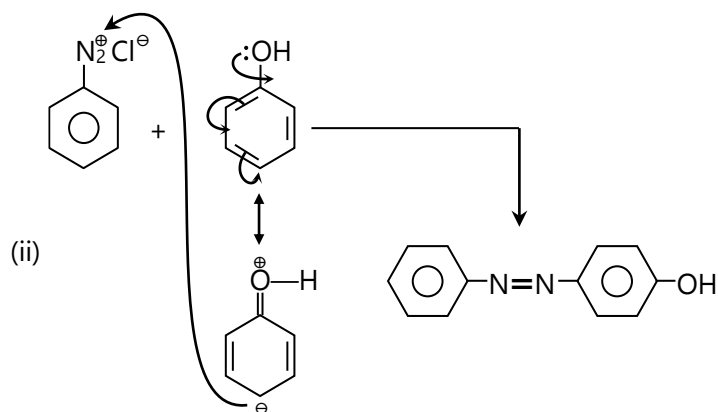
(ii) Refer Page-3 Gabriel Pthalimide synthesis

Sol.7 (a) Lone pair delocalised in aryl amines.



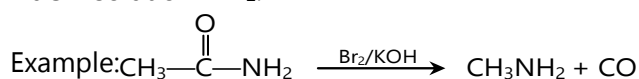
Sol.8 (i) Sandmeyer Reaction is used to synthesize aryl-halides from aryl amines.





Sol.9 (a) Refer to Sol.8 (ii)

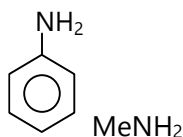
(b) The reaction involves the conversion of an amide into one carbon loss, by action of hypoactive NaOH solution + Br₂.



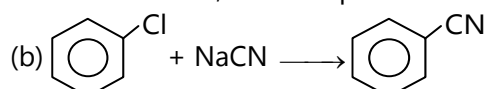
(c) Acetylation - 1° or 2° amines react with acetyl chloride or acetic anhydride to form acetyl derivatives.



Sol.10 (a) Aniline is a weaker base than methyl compound



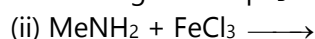
In case of aniline, the lone pair is delocalised on the ring and hence it is less basic.



Cl⁻ is a stronger base than CN⁻ hence the reaction can take place, + there is not sufficient +ve on the for nucleophilic substitute to take place.

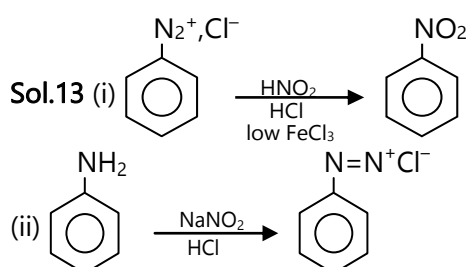
Sol.11 Refer to Sol.2 Ex.1

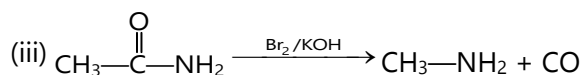
Sol.12 (i) Aniline is a weaker base as compared to methyl amine as lone pair of NH₂ is delocalised on the ring. Hence pK_B aniline > pK_B methyl amine.



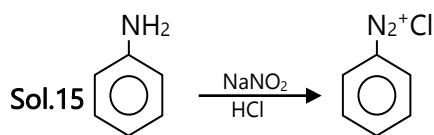
MeNH₂ is a good base in water, it reacts with FeCl₃ to form Fe(OH)₃ + MeNH₄⁺Cl⁻

(iii) Due to NH₂ group on aniline, there is extra e⁻ density on benzene ring. Hence, nucleophilic substitution does not take place.





Sol.14 Factual



Sol.16 (i) Refer to Sol.10 (i) Ex-1

(ii) Refer Sol.3 Ex-1

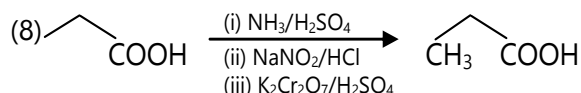
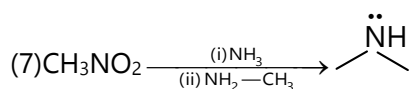
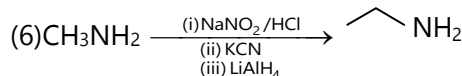
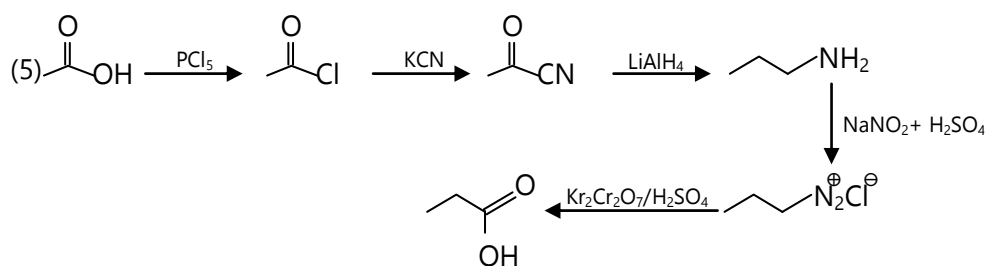
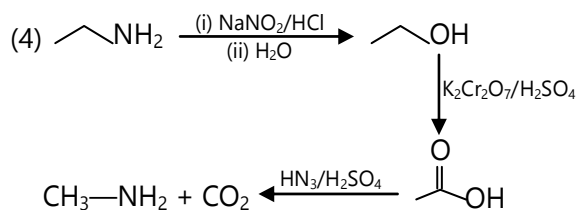
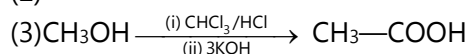
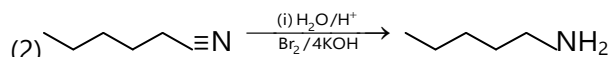
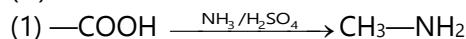
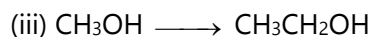
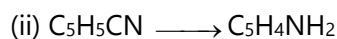
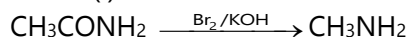
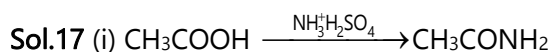
(iii) Refer Sol.12 (ii)

(iv)

(v) Refer Sol.12 (iii)

(vi) In aromatic amines, the \oplus charge is delocalised on the less electron -ve ring C- due to good resonance.

(vii) Due to the smaller size of 1° amine it easier to attack and hence. phthalimide synthesis is preferred for any amine.



Sol.18

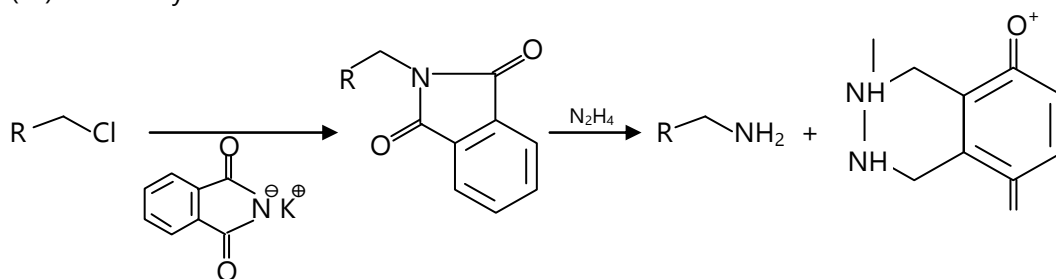
(iv) Any reactions which involves two or more equivalent of reactions for proceeding reaction are known as coupling reaction

Exp. Wurtz, Pinacol-pinacolone etc.

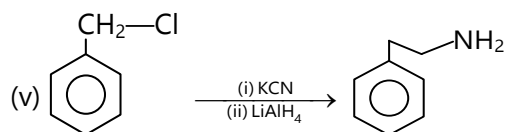
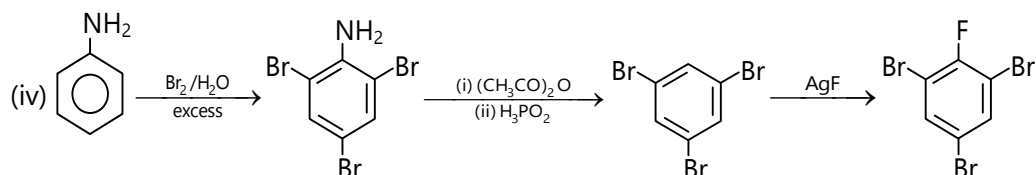
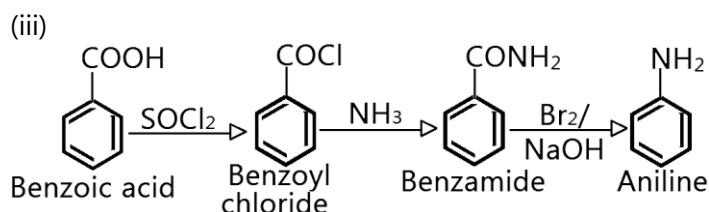
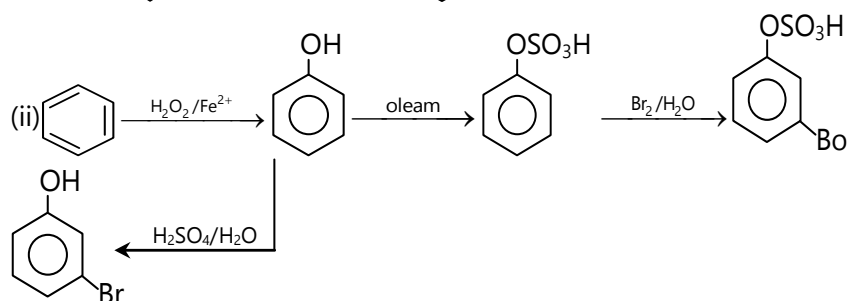
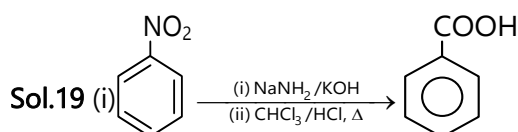
(v) addition of ammonia \longrightarrow Ammonolysis

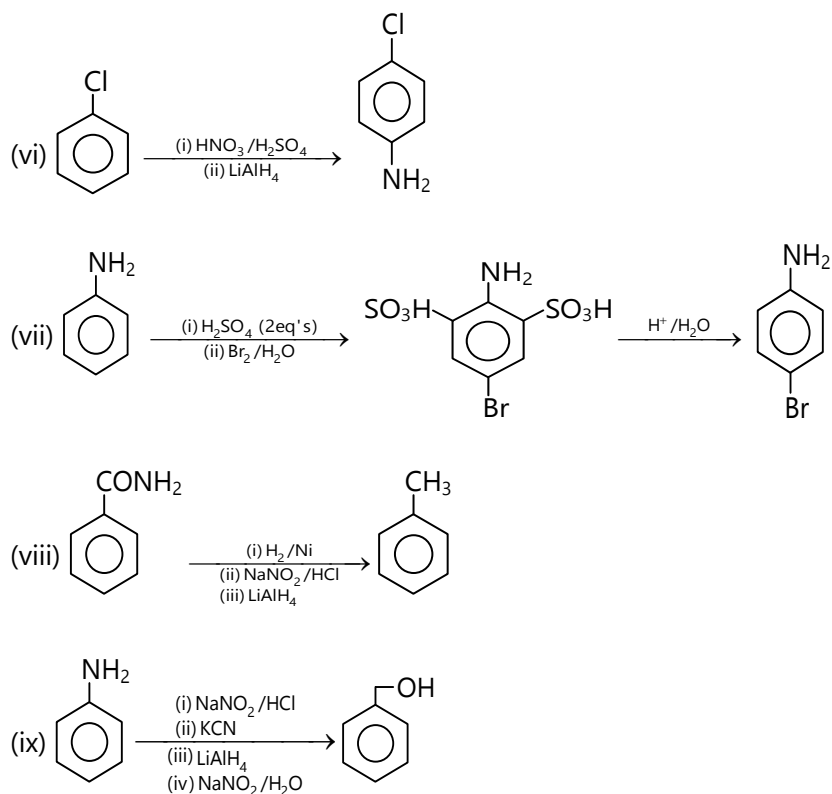
(vi) addition of acetyl group $(\text{CH}_3-\text{C}(=\text{O}))$ acetylation

(vii) Gabriel Synthesis:



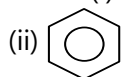
Test for 1° amines





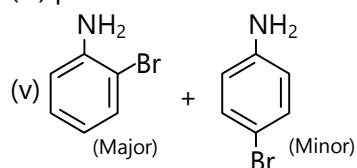
Sol.20 Refer Text for Curtius mechanism.

Sol.21 (i) $\text{ph}-\text{N}\equiv\text{C}$



(iii) Acid-base reaction $\text{ph}-\text{NH}_3^+ + \text{H}_2\text{SO}_4^-$

(iv) phOEt



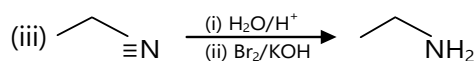
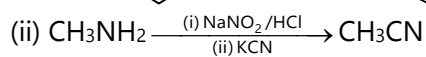
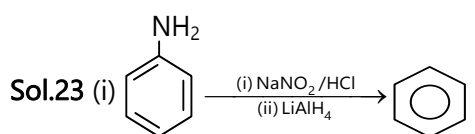
(vi) acetophenone

(vii) nitrobenzene

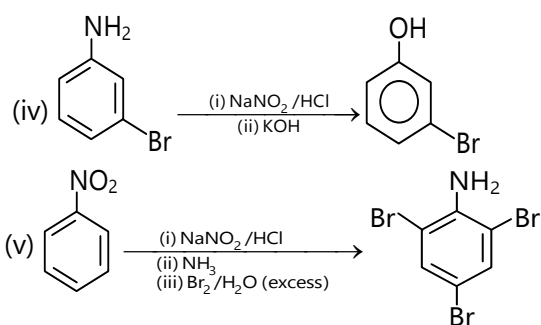
Sol.22 (i) Electronegativity of 'O' > 'N'

(ii) More surface area \Rightarrow more interaction b/w molecular \Rightarrow higher B.P.

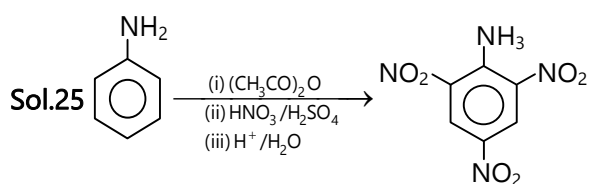
(iii) In aromatic amines, they have lone pair of N in conjugation with ring \Rightarrow less basic



Schmidt reaction



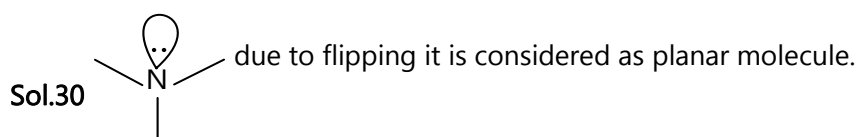
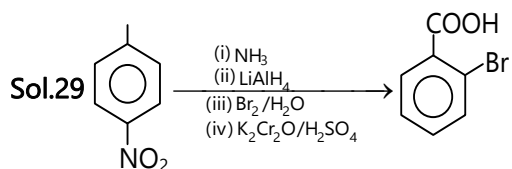
Sol.24 Intramolecular acid-base reactions of molecule (like some amine + carboxylic acid in same molecule)



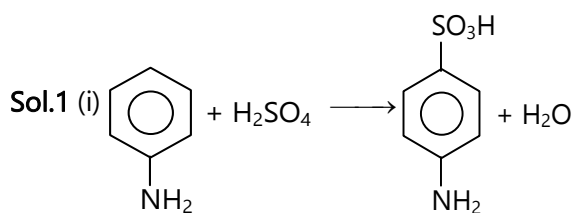
Sol.26 because carbocation intermediate in Friedel craft alkylation reach with l.p. of N in aniline

Sol.27 Same Ques. 18 (vii)

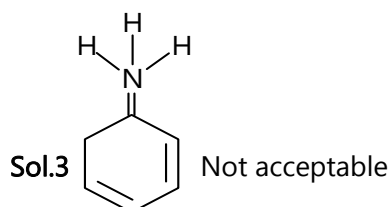
Sol.28 Same Ques. 18 (i)



EXERCISE – II JEE MAIN



Sol.2 The electron density on meta carbon is more than that on ortho and para positions. The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilized due to no mesomeric effect.



Nitrogen can't form 5 bonds

Sol.4 Order of basic strength
 $4 > 3 > 2 > 1$ Basic strength $\propto +I$ effect

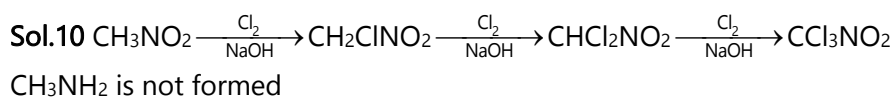
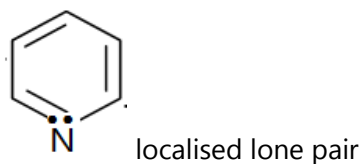
Sol.5 $1 > 2 > 3$

Sol.6 Primary amines gives carbylamine test.

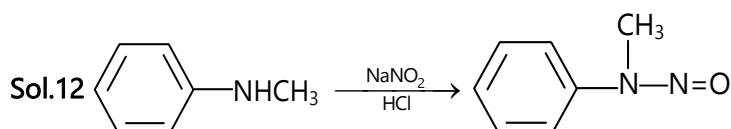
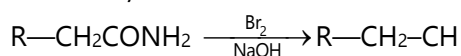
Sol.7 End product has a hydrophobic and a hydrophilic part.

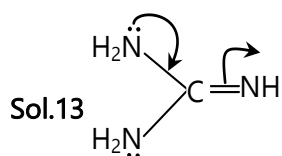
Sol.8 $s > t > p > \text{NH}_3$

Sol.9



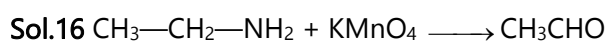
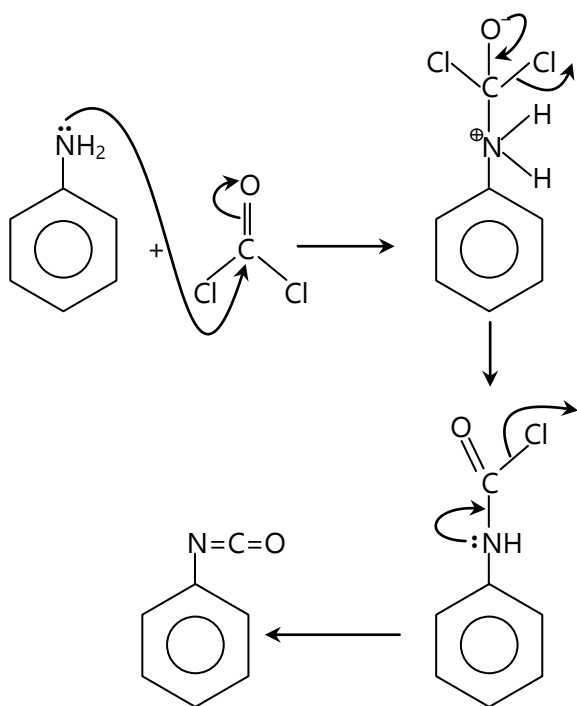
Sol.11 Br_2/NaOH



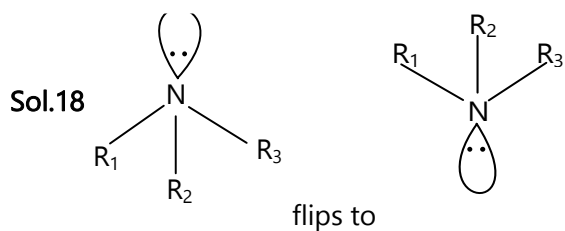


Sol.14 All of these
 $K_2Cr_2O_7$ is a strong oxidising agent.

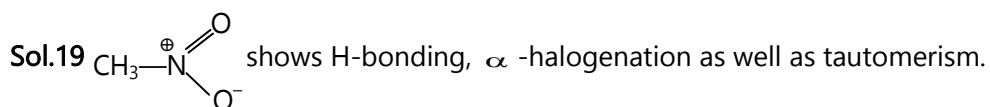
Sol.15



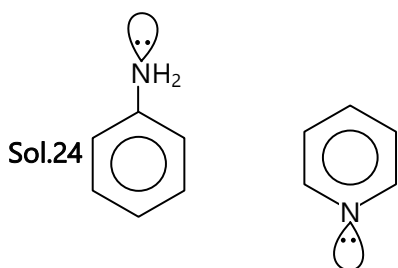
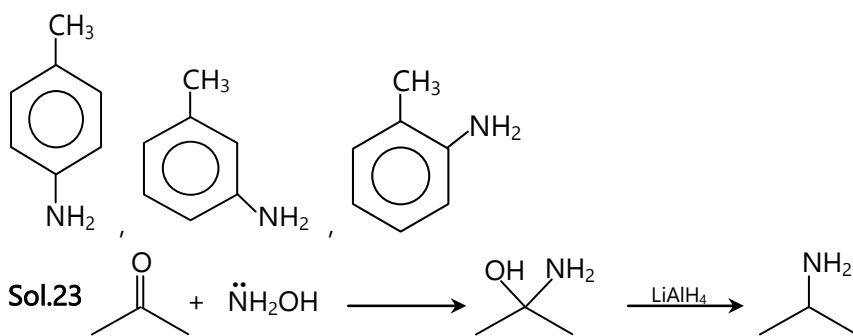
Sol.17 Baker-Mulliken's Test is a test for nitrocompounds.



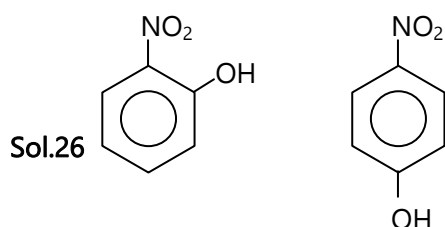
Due to flipping, tertiary amine is a racemic mixture.



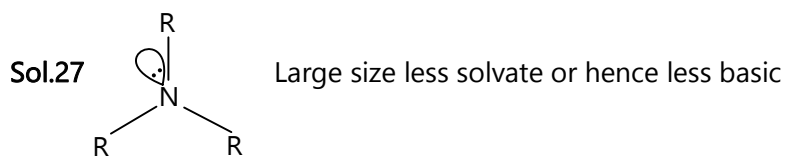
Sol.22



Sol.25 False lone pair is delocalised of Ph-NH₂ whereas its localised for aniline .
Self Explanatory

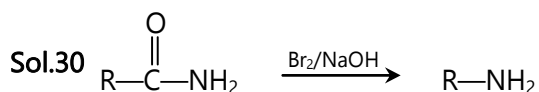


NO₂ has -M and -I effect. p-Nitro-phenol more acidic than ortho nitro phenol as o-nitro phenol intermolecular H-bonding where p-nitro phenol has inter molecular H-bond.



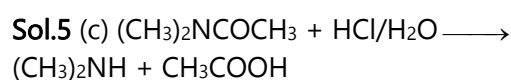
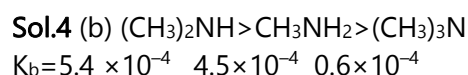
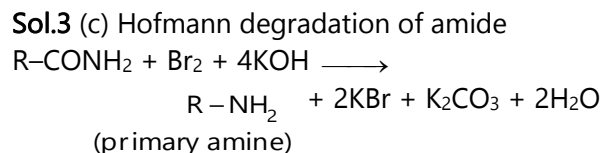
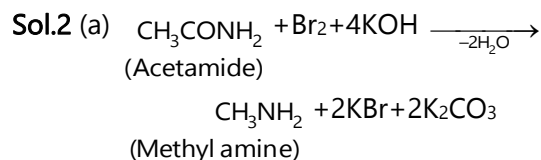
Sol.28 3° amine cannot be synthesised using Gabriel phthalimide

Sol.29 Both statements are true but 4-nitrochlorobenzene goes nucleophilic substitutions more readily than benzene due to the M-effect of nitro group 2 +ve charge is created on C attaches to Cl Molecule



Sol.31 Self explanatory (refer to theory of reaction)

PREVIOUS YEARS' QUESTIONS JEE MAIN



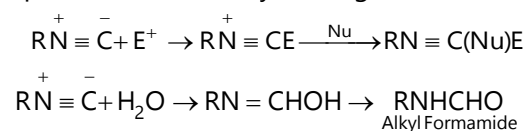
Sol.6 (c)

Sol.7 (a)
 Because OH^- is nucleophile.

Sol.8 (a) It is true that benzene diazonium chloride does not respond Lassaigne test of nitrogen because benzene diazonium chloride loses N_2 on slight heat and thus it can't react with sodium metal.

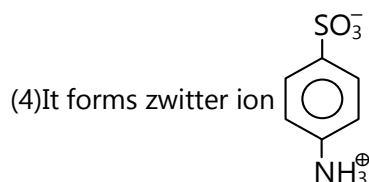
Sol.9 (a) Amines are basic due to the presence of a lone pair of electrons on nitrogen atom. The lone pair can be easily donated.

Sol.10 (a) In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.



Q.11 (a) self-explanatory

Sol.12 (b) Due to strong deactivation of benzene ring by $-\text{NO}_2$ group, nitrobenzene is often used as a solvent in Friedel-Craft's reaction.

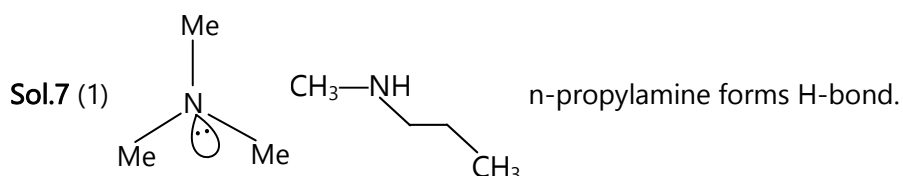


Sol.6 (1) Amine group in glycine is more basic.

(2) More equivalent resonance structures

(3) It stabilises the complex.

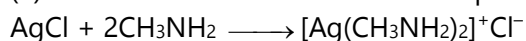
(4) Because of side products



(2) Steric hinderance in trimethylamine

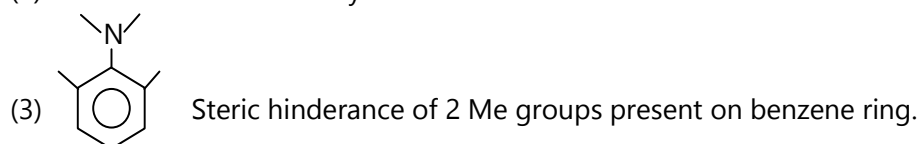
(3) Refer **Sol.7** (1)

(4) Due of formation of a soluble complex salt



Sol.8 (1) Ethylamine in aqueous solution reacts with ferric chloride to precipitate hydrated ferric acid.

(2) No N—H bond in tertiary amine.



(4) In (I) lone pair is localized

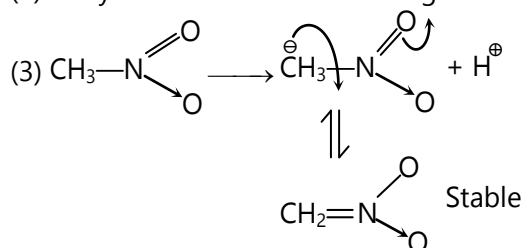
I effect of 'O' in (III)

In iv the lone pair is delocalised

I > II > III > IV

Sol.9 (1) Steric hinderance

(2) Isocyanides are stable in strong basic conditions, but they are sensitive of acids.



(4) Aniline forms a salt with AlCl_3 . Due to this nitrogen atom of aniline acquires a positive charge and hence acts as a strong deactivating group and doesn't allow the reaction to take place.

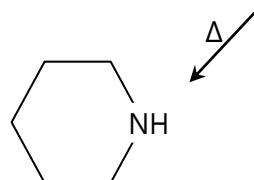
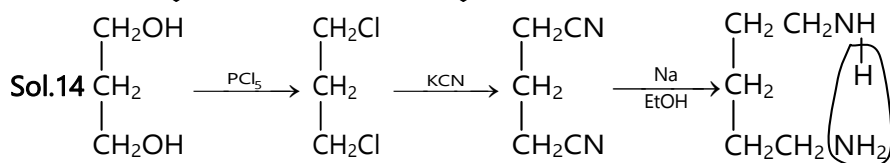
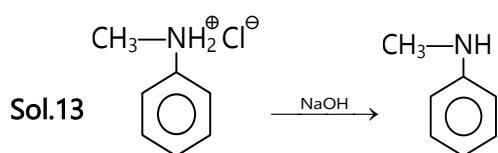
(5) The basicity of nitrogen in trimethylamine is greater.

Sol.10 Refer Answer key.

Sol.11 Refer Answer key.

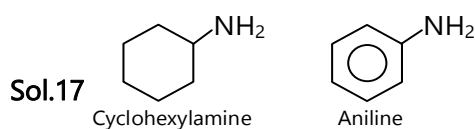
Amines and Aromatic Compounds Containing Nitrogen

Sol.12 $C_2H_5NH_2CH_3-CH_2-NH_2$



Sol.15 Refer Answer Key

Sol.16 Refer Answer Key

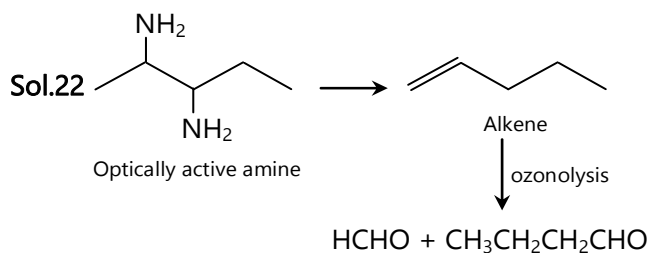
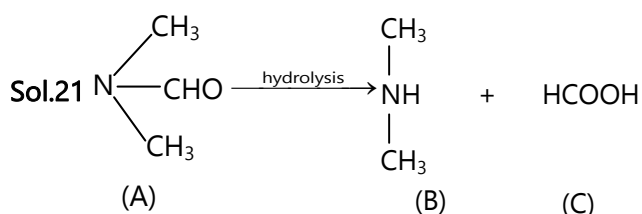


Lone pair of nitrogen in aniline is delocalized due to resonance.

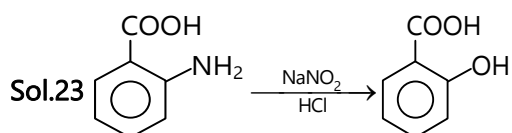
Sol.18 Use excess of ammonia to reduce the chances of reaction of 1° amine with alkyl halide to form 2° and 3° amines.

Sol.19 Amino group being activating group activates bromination of aniline and forms tribromoaniline.

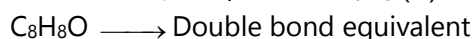
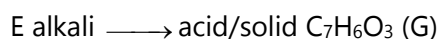
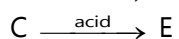
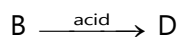
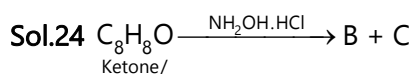
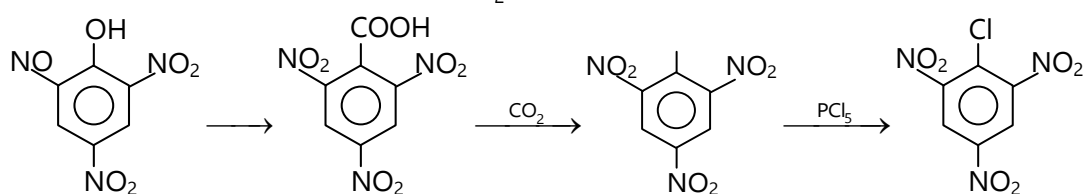
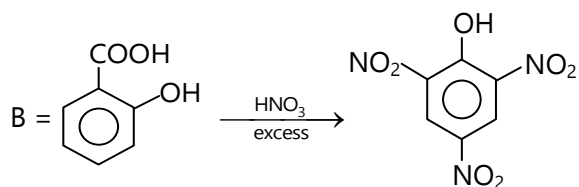
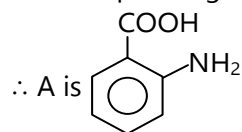
Sol.20 Although inductive effect of alkyl groups is greater in trimethylamine but the alkyl groups crowds the nitrogen atom and reduces its basicity.



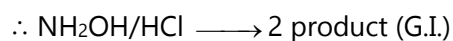
No, there is no structural isomer possible.



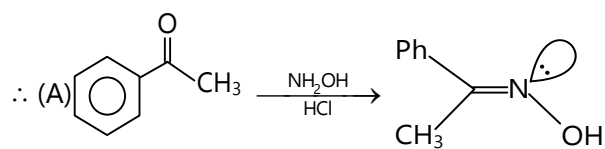
The compound gives \oplus ve less for NH_2 and COOH



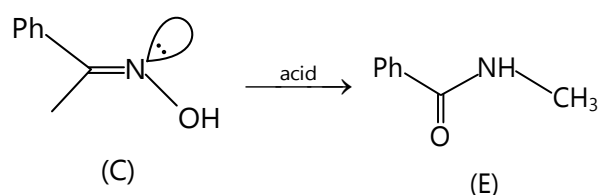
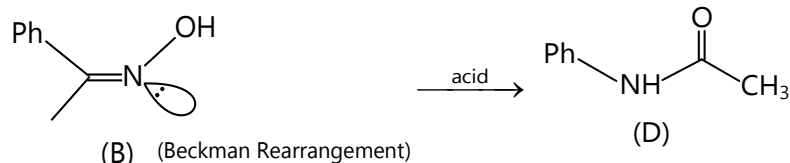
$\text{DBE} = \frac{1}{2} ((16+2)-8) = 5 \longrightarrow$ benzene ring and a π bond outside.

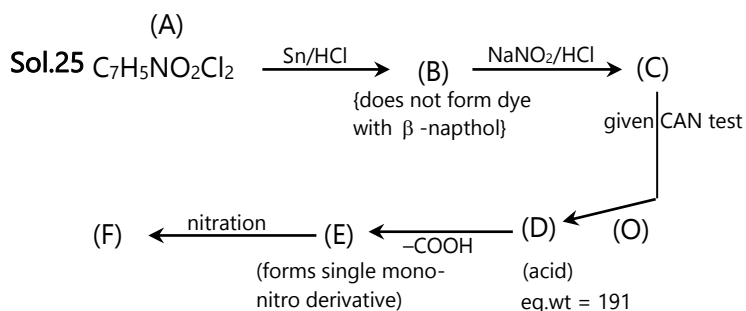
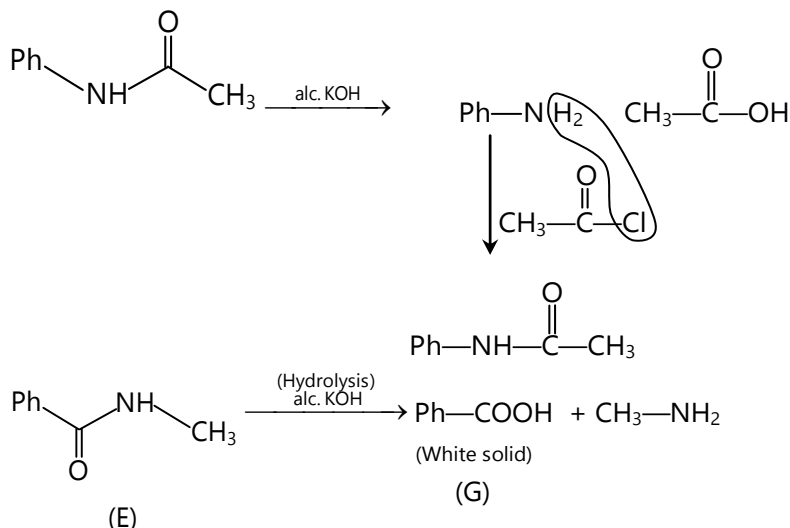


\therefore it is a ketone.



(2 G.I.)
cis and trans





Sol.26 $\therefore \text{NH}_4^+$

as gas is NH_3

M.W. 135 $\xrightarrow{-\text{NH}_2 + \text{OH}}$ B mole IRH

$\text{A} + \text{NaOH} \xrightarrow{\text{alc.}}$ $\text{R-CH}_2\text{COOH}$ \longrightarrow Mass of R =

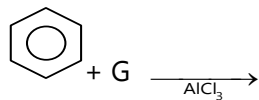
$\text{R-CH}_2\text{-NH}_2 \xrightarrow{\text{HNO}_2}$ RCOOH (B)

$\text{A} \xrightarrow{\text{Br}_2/\text{KOH}}$ C primary amine $\text{R-CH}_2\text{-NH}_2$

$\text{R-CH}_2\text{-CONH}_2$ (C) $\xrightarrow{\text{cold HNO}_2}$ (D) Primary amine $\xrightarrow{\text{red cold CAN}}$

$\text{E} \xrightarrow{\text{dil HCl}}$ F (mol. wt 136)

$\text{F} \xrightarrow{[\text{O}^y], \Delta}$ G



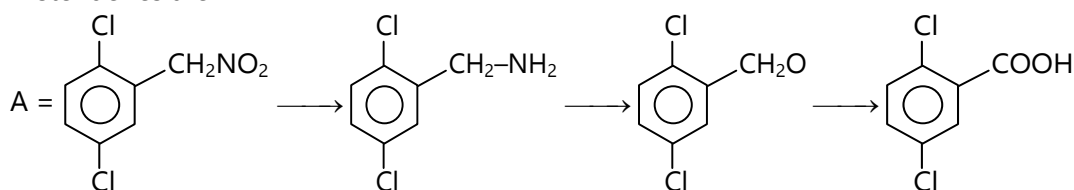
B = $\text{C}_7\text{H}_5\text{NH}_2\text{Cl}_2$ does not give compound B-does not form a dye with β -naphthol

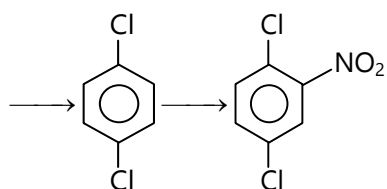
\therefore A is (C) is a primary alcohol.

as de-carboxylation gives single derivatives

\therefore Cl should be symmetrically oppositely placed.

\therefore stenderies are





Sol.28 Degree of unsaturated of A = 2 since A forms hydro alcohol sol, it contain both a basic and acidic functional group. It's most likely to be an amino acid. On decarboxylation, it forms an amine B, Degree of unsaturated of B = 0

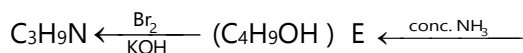
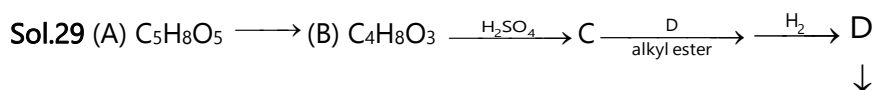
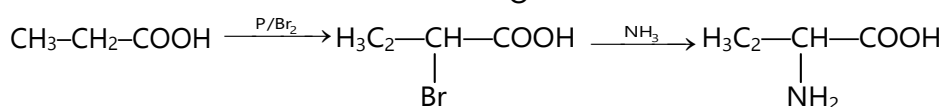
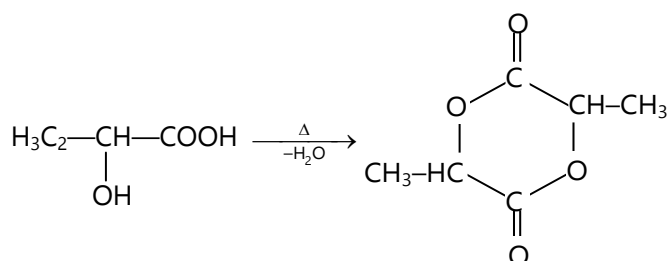
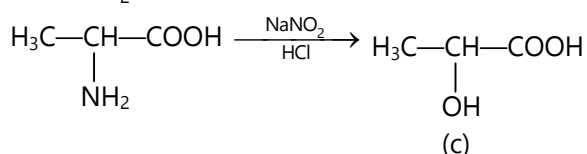
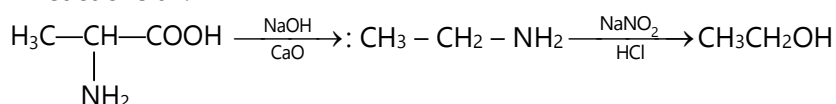
∴ B is saturated anil.

∴ B $\xrightarrow[\text{HCl}]{\text{NaNO}_2}$ give $\text{C}_2\text{H}_5\text{OH}$ (E)

∴ B is $\text{CH}_3\text{CH}_2\text{NH}_2$

$\xrightarrow[\text{HCl}]{\text{NaNO}_2}$ C (a hydroxyl acid) which pens cyclic di-ester on heating

∴ Reactions all:



degree of unsat

$$= 2 \times 5 + 2 - 8$$

$$= 4 - 2 = 2$$

EXERCISE – II JEE ADVANCED

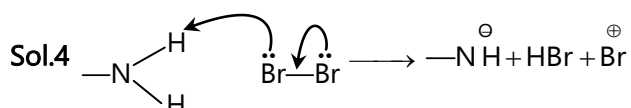
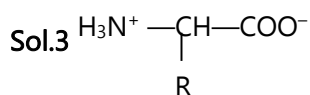
Sol.1 Propyne- Forms a precipitate with AgNO_3 in ethanol.

Ethyl Benzoate -Insoluble in water, but dissolves in aqueous NaOH upon heating

Acetaldehyde- Reduces Fehling's solution

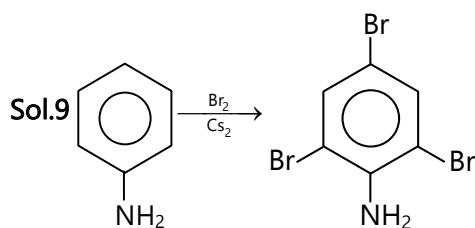
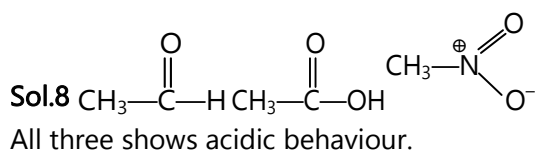
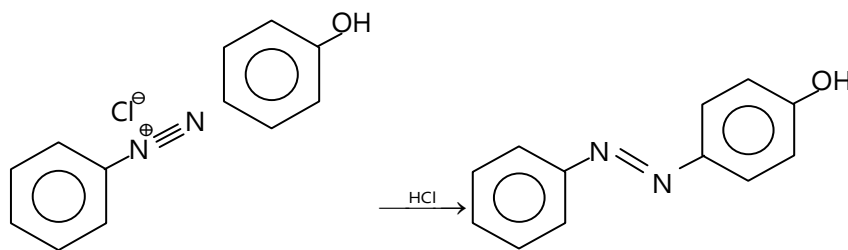
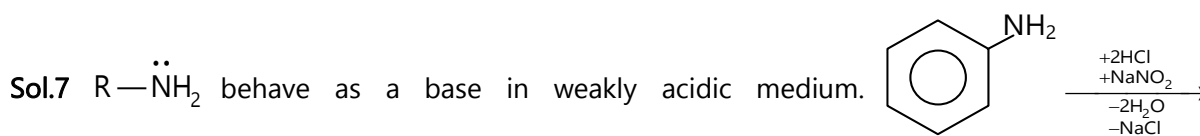
Aniline- Dissolves in dilute HCl in the cold and is reprecipitated by the addition of alkali.

Sol.2 Acetic acid

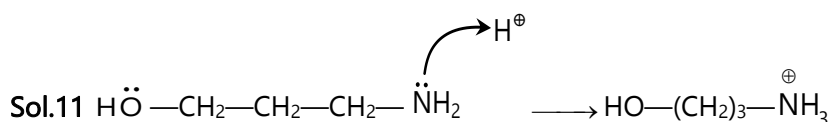


Sol.5 Ethylnitrile (CH_3CN)

Sol.6 The lone pair of electron on nitrogen atom in aniline is delocalized over aniline.

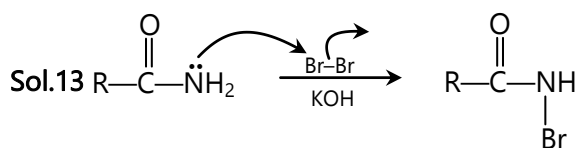


Sol.10 Gabriel-phthalimide synthesis.

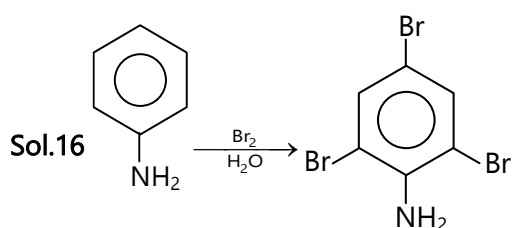
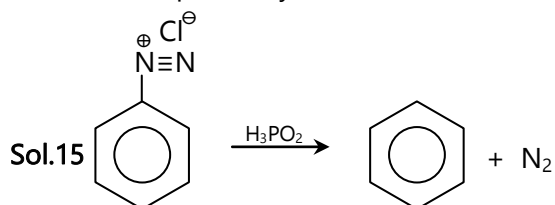


Sol.12 $2 > 1 > 3$

Consider inductive effect of primary, secondary and tertiary law.



Sol.14 Self-explanatory



Sol.17 Secondary amine

Sol.18 Trihalogenated amine and a primary amine

Comprehension:

Sol.19 $\text{NO}_2 \longrightarrow -\text{M}$ effect

$\text{CH}_3 \longrightarrow +\text{Z}$ effect

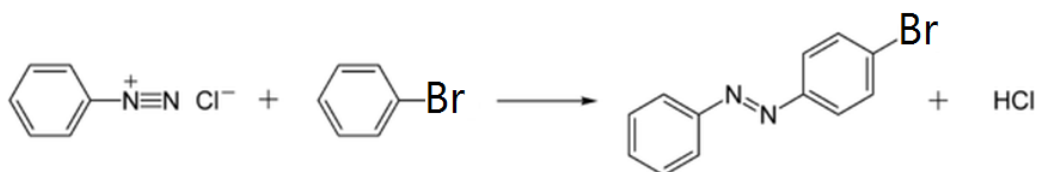
$\text{OCH}_3 \longrightarrow$ mid $+\text{M}$ effect

$\text{NMe}_2 \longrightarrow$ high $+\text{M}$ effect

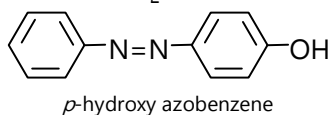
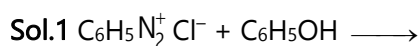
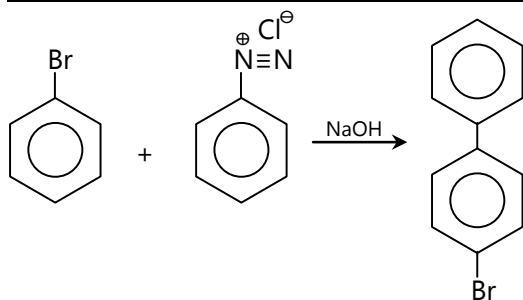
Sol.20 $-\text{I}$ effect of $-\text{OMe}$

Sol.21 $+\text{M}$ effect of $-\text{OMe}$ at para position

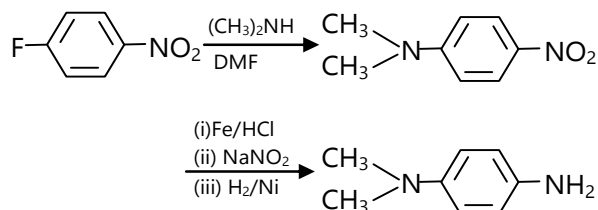
Sol.22



PREVIOUS YEARS' QUESTIONS JEE ADVANCED

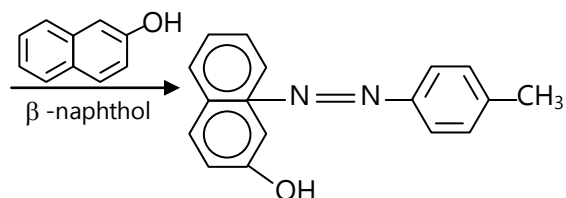
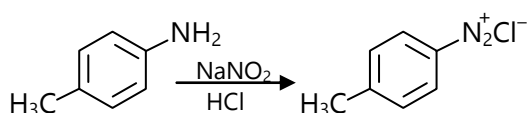
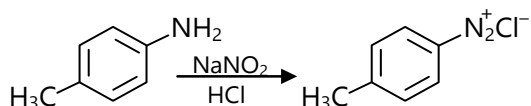


2.



Sol.3

As we know, benzenediazonium salt forms brilliant coloured dye with β -naphthol, the compound under consideration must be p -toluidine (c) as it is a primary aromatic amine. Primary aromatic amine, on treatment with $NaNO_2$ in dil. HCl forms the corresponding diazonium chloride salt.

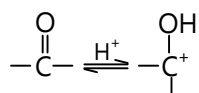


Match the columns

Sol. 4 Sodium fusion extract gives Prussian blue colouration, nitrogen and carbon both present in the compound.

Phenolic group and salt of carboxylic acid gives $FeCl_3$ test. Chloride salt gives white precipitate of $AgCl$ on treatment with $AgNO_3$.

Hydrazone formation occur effectively at $pH = 4.5$ The reaction proceeds in that condition only when H^+ concentration is just sufficient to activate the following enolization.

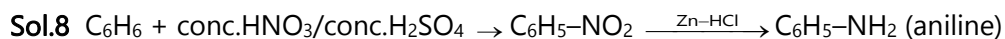
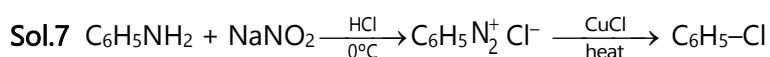
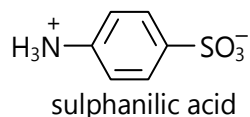


As H^+ concentration rises sufficiently, a large number of molecules of hydrazine gets converted into hydrazone ion which is not nucleophilic and reaction becomes impossible. Further low concentration of H^+ (in the case of 2,4-dinitrophenylhydrazinium bromide) is not effective to proceed elimination.

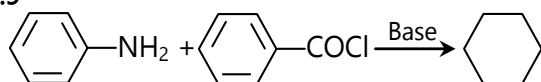
Fill in the Blanks

Sol.5 Aniline: It is a stronger base than either phenol or nitrobenzene.

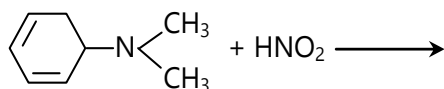
Sol.6 Zwitter ionic:



Sol.9



Sol.10



No reaction. Tertiary amine does not react with nitrous acid.

Empower your JEE Main & Advanced Preparation with PLANCESS PRODUCTS



Born from the stables of PlanceSS, PrepLane is an online test-preparation platform designed to give students all the practice they'll need to score better in a variety of entrance examinations including JEE, AIPMT and other examinations. Built with the idea of providing a personalised learning experience to every student, Preplane leverages cutting-edge analytics & adaptive learning technology to craft a custom learning experience for every learner.

FOUNDATION COURSE

Comprehensive package for IX & X aspirants prepared by National Olympiad Toppers.

- Study Material
- Video Lectures
- Assessment

AIPMT COURSE

A comprehensive self-study package for Pre-medical aspirants prepared by Qualified Medical Professionals and Top IITians.

- Study Material
- Video Lectures
- Assessment

JEE MAIN & ADVANCED COURSE

A comprehensive self-study package for Engineering aspirants prepared by Top 100 JEE Rankers.

- Study Material
- Video Lectures
- Assessment



To know more

☎ 022-6604-3411

✉ support@planceSS.com

🌐 www.PlanceSS.com

PlanceSS EduSolutions Pvt. Ltd.

A005/A006, Boomerang,

Chandivali - Chandivali Farm Rd,

Andheri (East), Mumbai - 400072, India,