25. AMINES AND AROMATIC COMPOUNDS CONTAINING NITROGEN

1. INTRODUCTION

(a) Alkyl derivatives of NH_3 are called Amines.

(b) If a hydrogen atom of NH_3 is replaced by an alkyl group, then it is called a primary amine and possesses $-NH_2$ (amino) group.

(c) If two hydrogen atoms of NH_3 are replaced then it is called a secondary amine and it posseses NH (Imino) group.

(d) If all hydrogen atoms of NH_3 are replaced then it is called a tertiary amine and has a nitrile N group.

(e) N is in sp^3 hybridisation and has tetrahedral geometry.

(f) The bond angle increases from ammonia to 3° amines. $NH_3(107^\circ) < RNH_2 < R_2NH < R_3N$

2. STRUCTURE AND BONDING

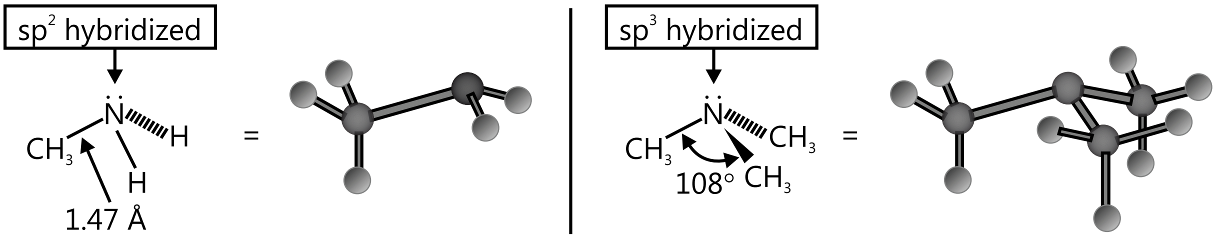


Figure 25.1: Hybridisation in primary and tertiary amine

(a) Trigonal pyramidal geometry

(b) High negative potential on N

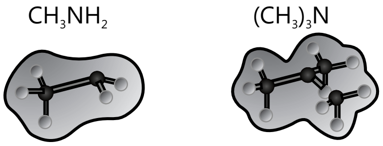


Figure 25.2: Bond Structure of primary and tertiary amine

(c) Amine N can be a stereogenic centre.

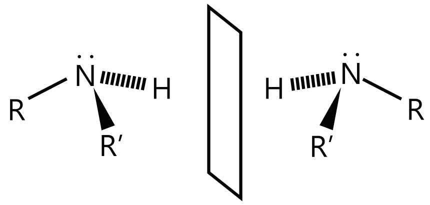


Figure 25.3: Amines as a Pair of enantiomer

(d) Enantiomers rapidly interconvert.

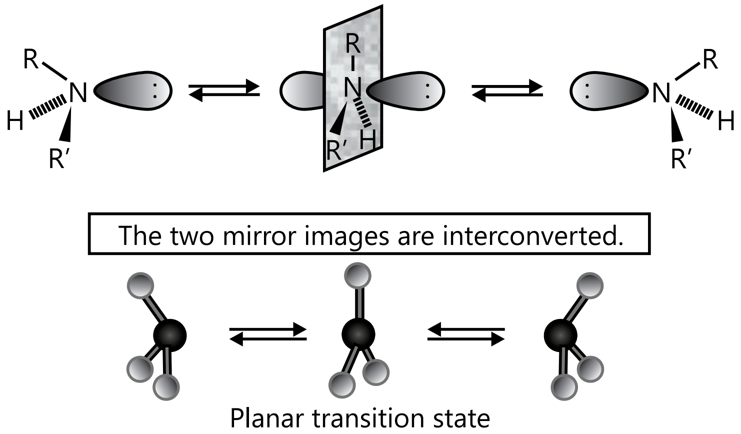


Figure 25.4: Interconversion of Enantiomers

(e) Enantiomers of quaternary ammonium salts:

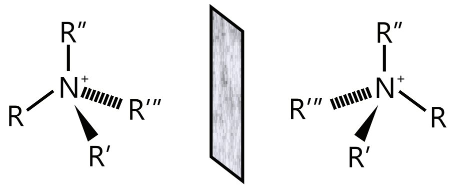


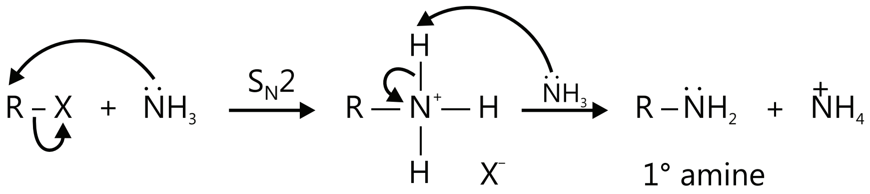
Figure 25.5: Isomerism shown by quaternary ammonium salt

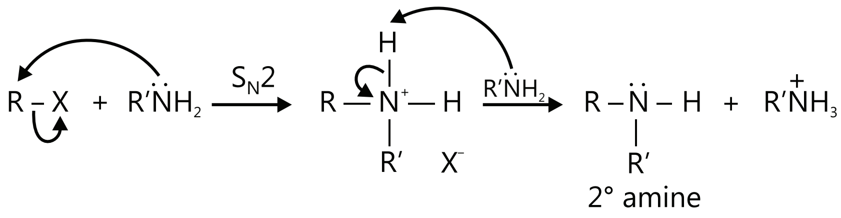
3. PREPARATION OF AMINES

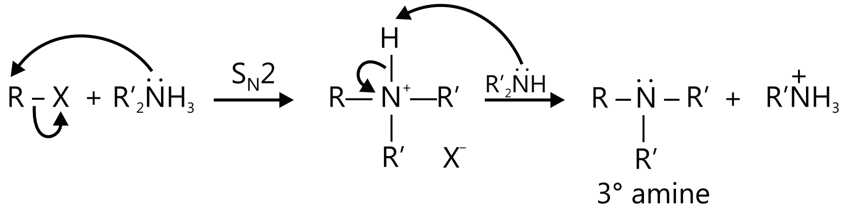
3.1 Nucleophilic Substitution

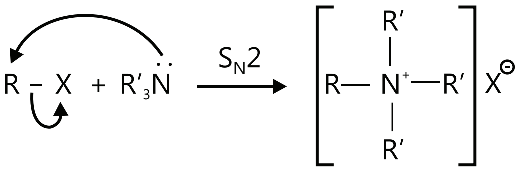
(a) Hofmann's Ammonolysis Reactions:

Direct Nucleophilic Substitution



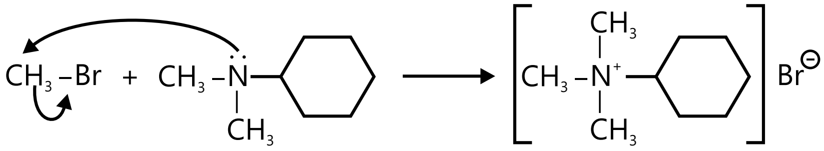






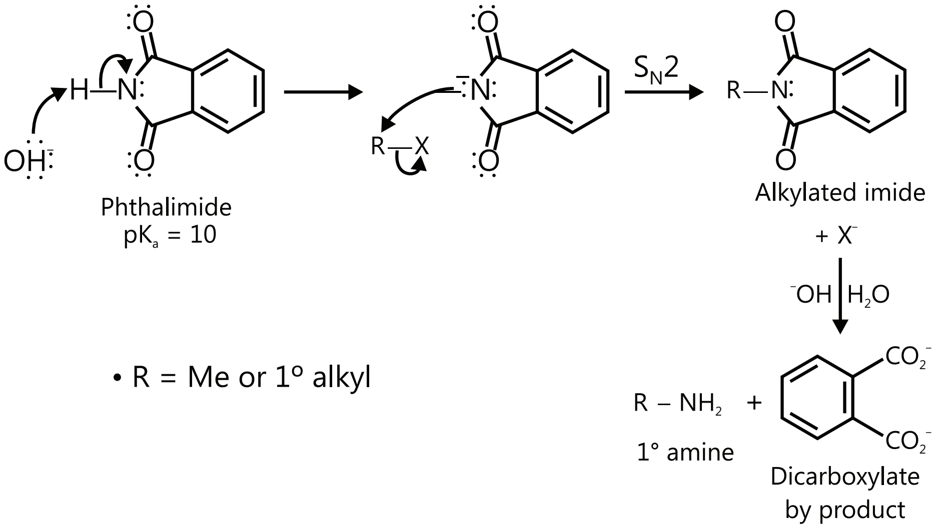
Drawback:

- **(i)** RX limited to methyl and 1° alkyl halides.
- **(ii)** Complicated by polyalkylation.
- **(iii)** Useful for preparing 1° amines and quaternary ammonium salts.



Quaternary ammonium salt

(b) Gabriel Phthalamide Synthesis:



- R = Me or 1° alkyl

3.2 Reduction of Nitrogen Containing Functional Groups

(a) From Nitro Componds

$$R-NO_2 \xrightarrow{\text{reduce}} R-NH_2$$

Reducing Agents:

(i) H_2/Pd-C

(ii) (1) Fe, HCl (2) OH^-

(iii) (1) Zn, or Sn, or $SnCl_2$ + HCl (2) OH^-

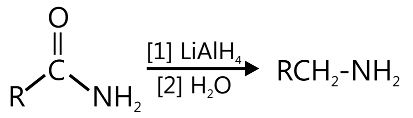
(b) From Nitriles

$$CH_3CH_2CH_2-C\equiv N \xrightarrow[2)\,H_2O]{1)\,LiAlH_4} CH_3CH_2CH_2-CH_2NH_2$$

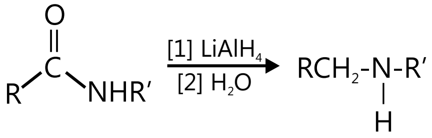
Nitriles from alkyl halides:

$$CH_3CH_2CH_2-Br \xrightarrow[S_N2]{NaCN} CH_3CH_2CH_2-C\equiv N$$

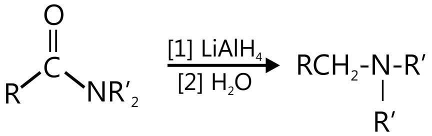
(c) From Amides



1° amide 1° amide



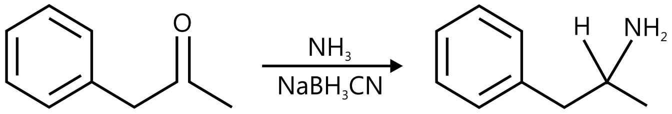
2° amide 2° amide



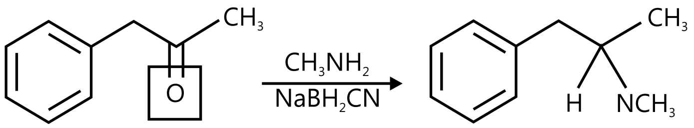
3° amide 3° amide

3.3 Reductive Amination

Examples:

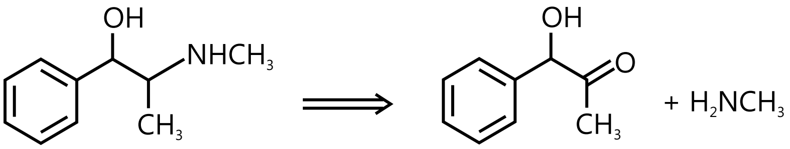


Amphetamine
a powerful stimulant



2° amine
Methamphetamine

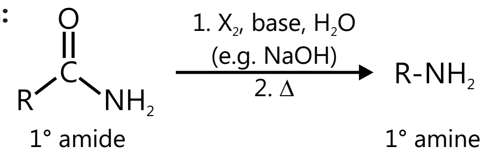
Retrosynthetic Analysis:



2° amine
Methamphetamine

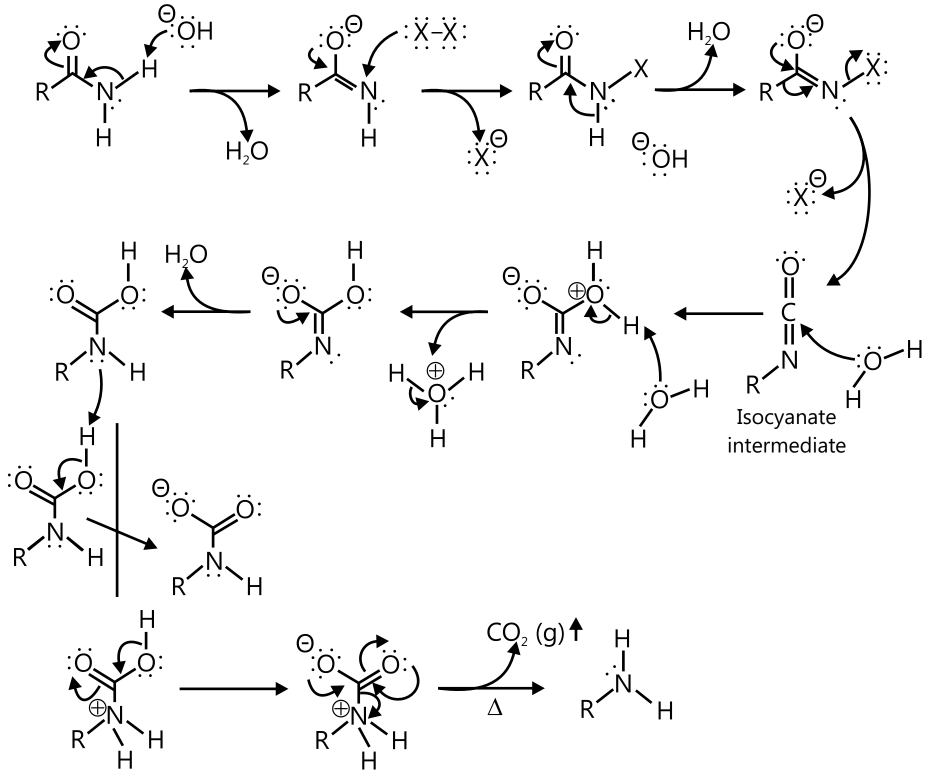
3.4 Rearrangement Reactions

(a) Hofmann's Bromamide Reaction:

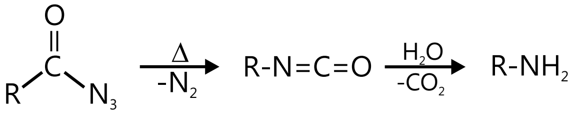


X = Cl, Br

Mechanism:

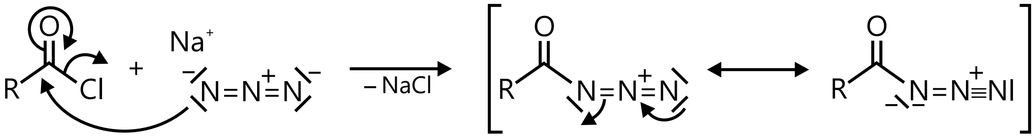


(b) Curtius Rearrangement:

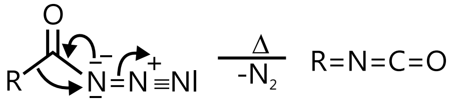


Mechanism:

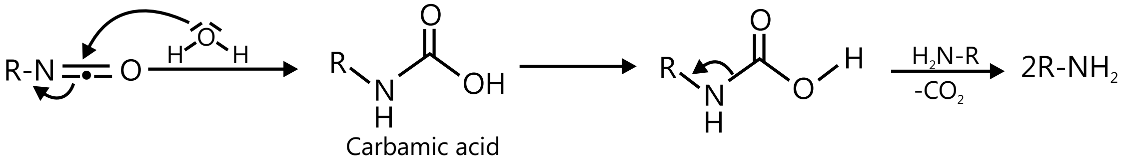
Step 1 Preparation of azides:



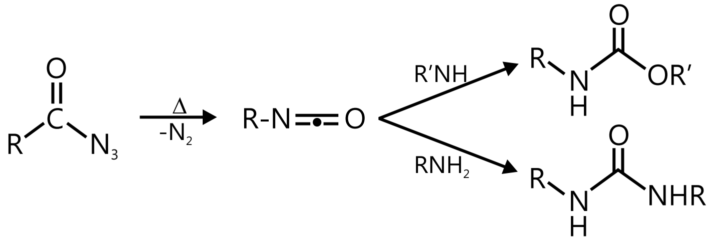
Step 2 Decomposition:



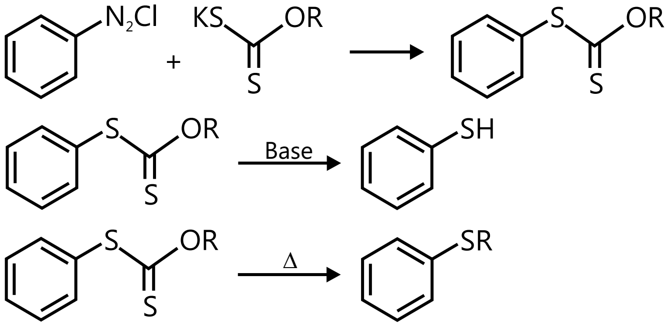
Reaction with water to the unstable carbamic acid derivative which will undergo spontaneous decarboxylation:



Isocyanates are versatile starting materials:

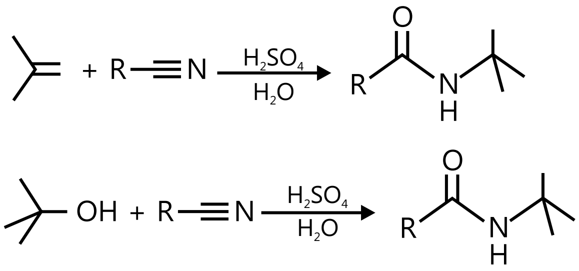


(c) Leuckart Thiophenol Reaction:



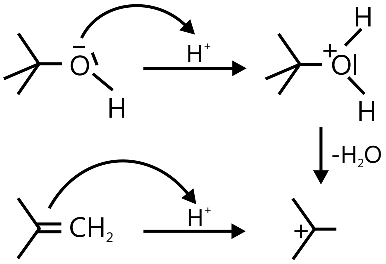
The Leuckart Thiophenol Reaction allows the preparation of thiophenols and corresponding thioethers from anilines or their corresponding diazonium salts. The first step of the reaction of an aryl diazonium salt with a potassium alkyl xanthate to give an aryl xanthate, which affords an aryl mercaptan upon the basic hydrolysis or an aryl thioether upon warming.

(d) Ritter Reaction:

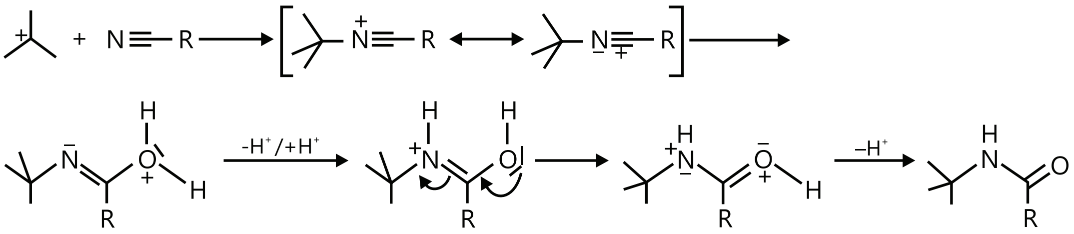


The acid-induced nucleophilic addition of a nitrile to a carbonium ion, followed by the hydrolysis to the corresponding amide.

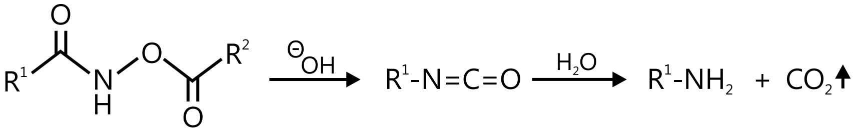
Mechanism of the Ritter Reaction: Any substrate capable of generating a stable carbonium ion is a suitable starting material; primary alcohols do not react under these conditions, with the exception of benzylic alcohols.



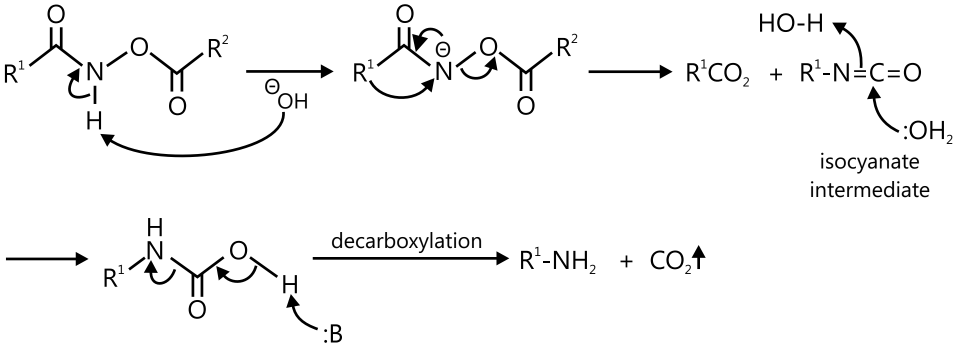
The carbonium ion adds to the nitrile nitrogen to give a nitrilium ion intermediate, which undergoes hydrolysis to the corresponding amide upon the aqueous work-up.



(e) Lossen's Rearrangement:


$$R^1C(=O)NHOC(=O)R^2 \xrightarrow{^{\ominus}OH} R^1\text{-}N=C=O \xrightarrow{H_2O} R^1\text{-}NH_2 + CO_2\uparrow$$

Mechanism:



(f) Claisen Schmidt rearrangement:

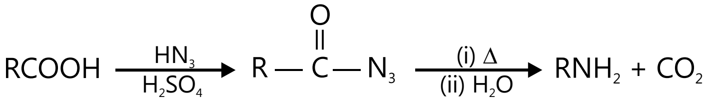

$$RCOOH \xrightarrow[H_2SO_4]{HN_3} R-\overset{\overset{O}{\parallel}}{C}-N_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) }\Delta} RNH_2 + CO_2$$

Illustration 1: Prepare n-butylamine by Gabriel synthesis. **(JEE MAIN)**

Sol: This method is mainly used in preparation of Primary amine by use of alkyl halide and Potassium phthalimide. After the attack of alkyl halide, Potassium phthalimide no longer behaves as a nucleophile. Product is cleaved by reaction with base or hydrazine, which leads to a stable cyclic product. The by-product of this reaction is an acid.

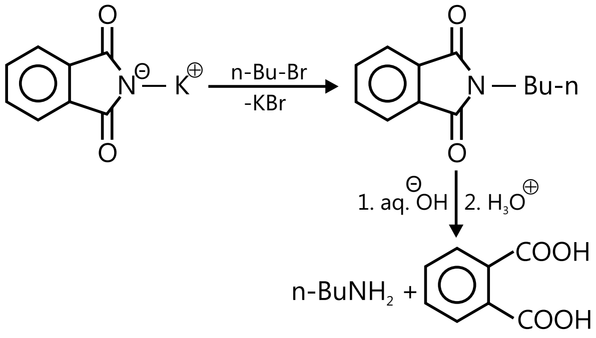
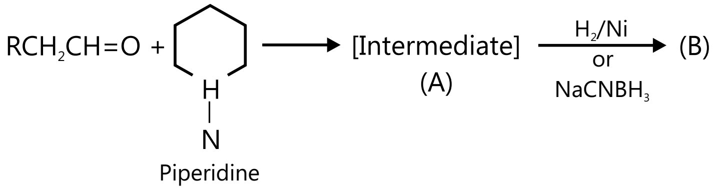


Illustration 2: **(JEE MAIN)**



Sol: Reaction between aldehyde and piperidine proceed via formation of carbinolamine which gets converted to Iminium ion intermediate. On reduction with Raney Ni, tertiary amine is formed.

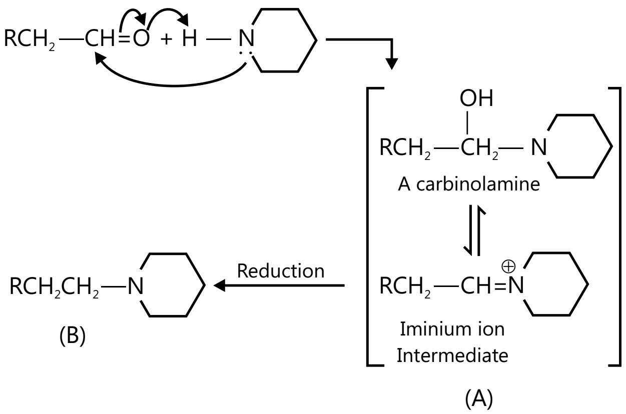
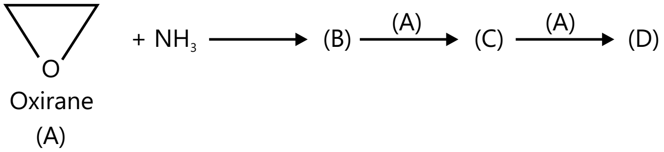


Illustration 3: Complete the following reactions: **(JEE ADVANCED)**



Sol:

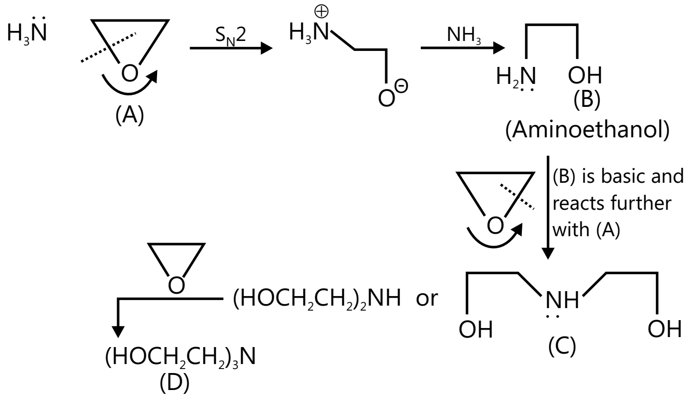
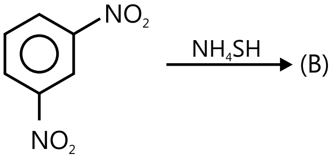


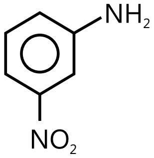
Illustration 4: Complete the following: **(JEE ADVANCED)**



(A)

Sol: It is an example of region selective reaction. One of the nitro group preferentially gets reduced by NH_4SH $(NH_4)_2S$ or NH_4SH reduces only one nitro group. (B) is

B is



4. PHYSICAL PROPERTIES OF AMINES

(a) Unlike most other organic compounds, amines are far more soluble in water, this is because all amines form a stronger H–bond with water.

(b) Like ammonia, amines are polar compounds and apart from 3° amines, they can form intermolecular H–bonds that's why they have higher b.p.s'.

(c) The boiling points of amines are lesser than of alcohols and acids of comparable mol. weight because H–bonding in amines is less pronounced in 1° and 2° than that in alcohols and carboxylic acids. This is because nitrogen is less electronegative than oxygen.

(d) Boiling point of 1°, 2° and 3° amines follow the order.

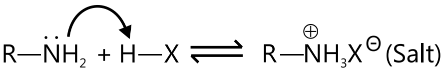
1° > 2° > 3° amine

(e) Solubility in water follow the order.

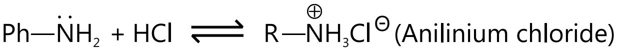
1° > 2° > 3° amine

This is all due to H–Bonding.

Basicity of Amines: Due to basic nature, they react with acids to form salts.



$$R—\ddot{N}H_2 + H—X \rightleftharpoons R—\overset{\oplus}{N}H_3X^{\ominus}\text{(Salt)}$$



$$Ph—\ddot{N}H_2 + HCl \rightleftharpoons R—\overset{\oplus}{N}H_3Cl^{\ominus}\text{(Anilinium chloride)}$$

Amine salts on treatment with bases such as NaOH regenerate the parent amine.

$$\overset{+}{R}NH_3X^- + \overset{-}{O}H \longrightarrow R\ddot{N}H_2 + H_2O + \overset{-}{X}$$

Relative Basicity of Amines: Compare basicities by using conjugate acid pK_a values.

(a) An Amine and Ammonia

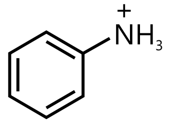
$$H-NH_3^+ \quad pK_a = 9.3 \quad NH_3 \text{ (weaker base)}$$

$$CH_3CH_2-NH_3^+ \quad pK_a = 10.8 \quad CH_3CH_2NH_2 \ \text{(strong base)}$$

(i) Alkyl amines are stronger bases than NH_3

(ii) Electron-donating alkyl group increase the electron density on N.

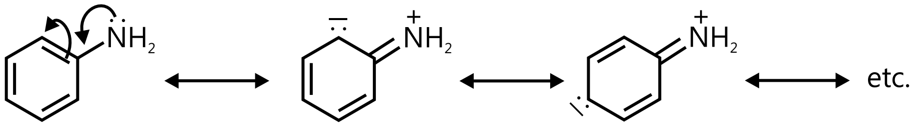
(b) An Alkylamine and an Arylamine



$CH_3CH_3\overset{+}{N}H_3$

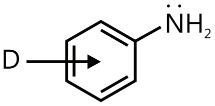
$pK_a = 4.6$ $pK_a = 10.8$

Aniline is a weaker base that ethylamine. Why?



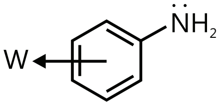
$CH_3CH_2\ddot{N}H_2$ localized lone pair

(i) Electron donors increase basicity.



D can be $-NH_2$, -OH, -OR, -NHCOR, -R

(ii) Electron withdrawers decrease basicity.



W can be -X, -CHO, -COR, -COOR,
-COOH, -CN, $-SO_2H$, $-NO_2$, $-NR_3$

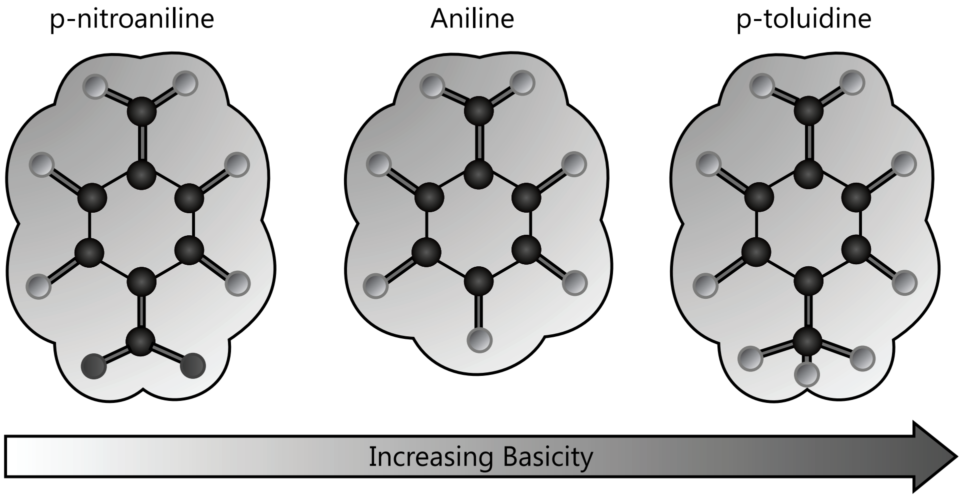
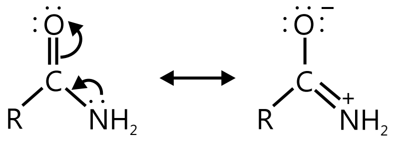


Figure 25.6: Order of Relative basicity of Amine

Order of Relative basicity of Amine

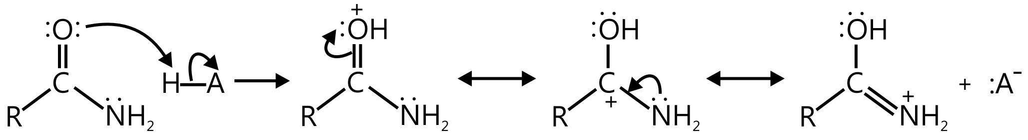
(c) An Alkylamine and an Amide

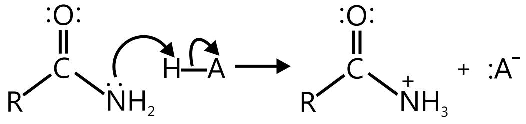


Lone pair on N is resonance delocalized.

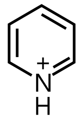
(i) Amides are less basic than alkyl amines.

(ii) Preferred site of protonation is on oxygen.

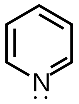




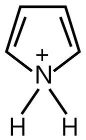
(d) Heterocyclic Aromatic Amines



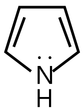
pKa = 5.3



pyridine



$pK_a = 0$

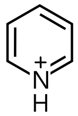


pyrrole

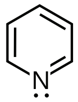
(i) Pyridine – stronger base – lone pair localized

(ii) Pyrrole – weaker base – lone pair delocalized

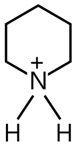
(e) Effect of Hybridization



$pK_a = 5.3$

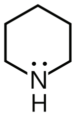


pyridine



$pK_a = 11.1$

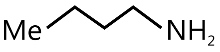
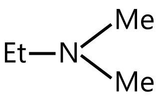
piperidine



(i) Pyridine – weaker base – lone pair in sp^2 orbital

(ii) Piperidine – stronger base – lone pair in sp^3 orbital

Illustration 5: Give the decreasing order of boiling points for the following: **(JEE MAIN)**

I. Et_2NH II.  III.  $Et-N<^{Me}_{Me}$

Sol: Extent of hydrogen bonding decreases in the order (1° > 2° > 3° amine) thus boiling point also decreases in the order (1° > 2° > 3° amine)

(II) > (I) > (III) (1° > 2° > 3° amine)

Illustration 6: Arrange the following in the decreasing order of their basic strength: **(JEE MAIN)**

a. i. $PhNH_2$ ii. $EtNH_2$ iii. Et_2NH iv. NH_3

b. i. $EtNH_2$ ii. $PhNH_2$ iii. NH_3 iv. $PhCH_2NH_2$ v. Et_2N

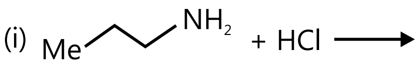
Sol: Extent of hydrogen bonding decreases in the order (1° > 2° > 3° amine) thus boiling point also decreases in the order (1° > 2° > 3° amine)

a. Aliphatic 2° amine > Aliphatic 1° amine > NH_3: Aromatic amine

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

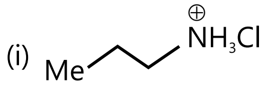
b. (v) > (i) > (iv) > (iii) > (ii)

Illustration 7: Complete the following acid-base reaction and name the products. **(JEE ADVANCED)**

(i) 

(ii) $Et_3N + HCl \longrightarrow$

Sol: (i)



(Propanammonium chloride)

(ii) $Et_3N^+Cl^-$ (Triethylammonium chloride)

PLANCESS CONCEPTS

Preparation of amines:

- reduction of nitro compounds to amines by metals(Fe, Sn, Zn) in dil HCl or $SnCl_2$ or by hydrogen in presence of Ni, Pt, Pd.

  Misconception: $LiAlH_4$ doesn't reduce the nitro compounds to amines. Instead it reduces it to R-N=N-R.

- Amines can also be prepared by the Hoffmann ammonolysis reaction which is a S_N2 reaction. NH_3 reacts with the alkyl halide to give primary halides which in turn react with more alkyl halides to give 2° and 3 amines and then gives 4° ammonium salts.

  Exception: Hoffmann ammonolysis reaction cannot be used to prepare aromatic amines.

- Amines can also be produced by the reduction of nitriles with $LiAlH_4$ or catalytic hydrogenation. But note that only primary amines can be produced.

  Misconception: Besides $NaBH_4$ does not give primary amines.

- Amines can also be prepared by the reduction of amides, oximes and azides by $LiAlH_4$. But again only primary amines can be produced by this method.

- Primary amines can also be produced by Gabriel phthalamide synthesis. In this pthalic anhydride is converted to phthalamide which is then treated with an alkyl halide to give N-alkyl pthalamide. Finally it is treated with hydrazine to give a primary amine.

  Exception: primary aromatic amines cannot be prepared by Gabriel phthalamide synthesis because aromatic halide doesn't give a substitution reaction with phthalamide.

- Primary amines can be prepared by Hoffmann bromamide reaction where the amide is treated with Br_2 in the presence of an alkali to give a primary amine. The intermediate species is nitrene which undergoes intra rearrangement to give RNH_2.

- Some other methods to prepare primary amines are Lossen rearrangement, Curtius rearrangement, Claisen-Schmidt rearrangement. All have one thing in common, i.e., they proceed through the nitrene mechanism.

- Amines can also be produced by the reductive amination of carbonyl compounds. Carbonyl compounds give imines which on reduction with H_2 in presence of Ni gives an amine. Aldehydes give primary amines and ketones give secondary amines.

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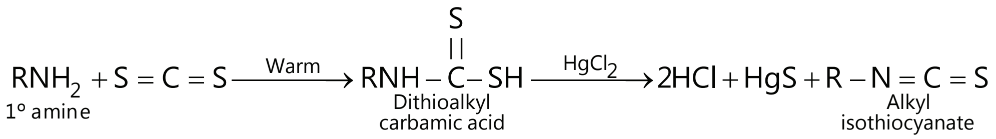
5. VARIOUS TESTS FOR AMINES

(a) Hofmann Mustard Oil Reaction (Test for 1° Amines)



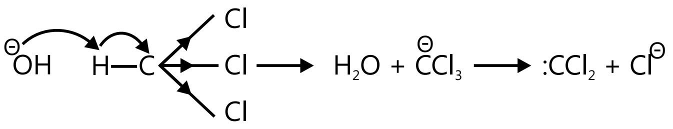
$$\underset{\text{1° amine}}{RNH_2} + S=C=S \xrightarrow{\text{Warm}} \underset{\substack{\text{Dithioalkyl}\\\text{carbamic acid}}}{RNH-\overset{\overset{\displaystyle S}{||}}{C}-SH} \xrightarrow{HgCl_2} 2HCl + HgS + \underset{\substack{\text{Alkyl}\\\text{isothiocyanate}}}{R-N=C=S}$$

Alkyl isothiocyanates gives a smell like that a mustard oil and this is used as a test for 1° amines.

(b) Carbylamine Reaction (Test for 1° Amine): It consists of heating a mixture of 1° aliphatic or aromatic amines and chloroform with alcoholic KOH solution. The reaction proceeds via carbene mechanism.

$$R-NH_2 + CHCl_3 + 3KOH\ (\text{Alcoholic}) \xrightarrow{\Delta} R-N^+\equiv C^- + 3KCl + 3H_2O$$

Mechanism:



$$R-NH_2 + :CCl_2 \longrightarrow RN^+\equiv C^- + 2HCl$$

Isocyanides have a very offensive smell. So, this reaction is use to distinguish 1° amines.

(c) Hinsberg's Test (for distinguishing 1°, 2° and 3° amines): Three classes of amines are distinguished by Hinsberg reagent test. The Hinsberg reagent is a benzene sulphonyl chloride ($C_6H_5SO_2Cl$).

(d) Reaction of Hinsberg Reagent with Primary Amines: A primary amine forms a precipitate of N-alkyl benzene sulphonamide with Hinsberg reagent. This precipitate is soluble in alkali.

$$RNH_2\ (\text{primary amine}) + C_6H_5SO_2Cl\ (\text{Hinsberg reagent}) \longrightarrow R-NH-SO_2-C_6H_5 \xrightarrow{NaOH} R-N^-Na^+-SO_2C_6H_5\ (\text{soluble})$$

(e) Reaction of Hinsberg Reagent with a Secondary Amine: Secondary amine reacts with the Hinsberg reagent to form a precipitate N,N-dialkyl benzene sulphonamide. But this precipitate is insoluble in alkalis.

$$R_2NH\ (\text{secondary amine}) + C_6H_5SO_2Cl\ (\text{Hinsberg reagent}) \longrightarrow \underset{\text{(Precipitate)}}{R_2NSO_2C_6H_5} \xrightarrow{NaOH} \text{Insoluble (no reaction)}$$

(f) Reaction of Hinsberg Reagent with a Tertiary Amine: Tertiary amines do not react with Hinsberg reagent.

$$R_3N\ (\text{Tertiary amine}) + C_6H_5SO_2Cl\ (\text{Hinsberg reagent}) \longrightarrow \text{No reaction}$$

(g) Reaction with Nitrous acid (For Distinguishing 1°, 2° and 3° amines): Nitrous acid (HNO_2 or HONO) reacts with aliphatic amines in a fashion that provides a useful test for distinguishing, primary, secondary and tertiary amines.

$$1^\circ\text{-Amines} + \text{HONO (cold acidic solution)} \longrightarrow \text{Nitrogen Gas Evolution from a Clear Solution}$$

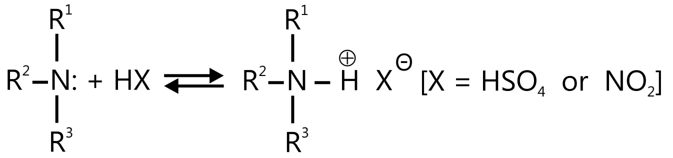
$$2^\circ\text{-Amines} + \text{HONO (cold acidic solution)} \longrightarrow \text{An Insoluble Oil (N-Nitrosamine)}$$

$$3^\circ\text{-Amines} + \text{HONO (cold acidic solution)} \longrightarrow \text{A Clear Solution (Ammonium Salt Formation)}$$

Nitrous acid is a Bronsted acid of moderate strength ($pK_a = 3.3$). Because it is insoluble, it is prepared immediately before use in the following manner.

$$NaNO_2 + H_2SO_4 \xrightarrow{H_2O,\ 0^\circ} H-\underset{..}{\ddot{O}}-\ddot{N}=\underset{..}{\ddot{O}} + NaHSO_4$$

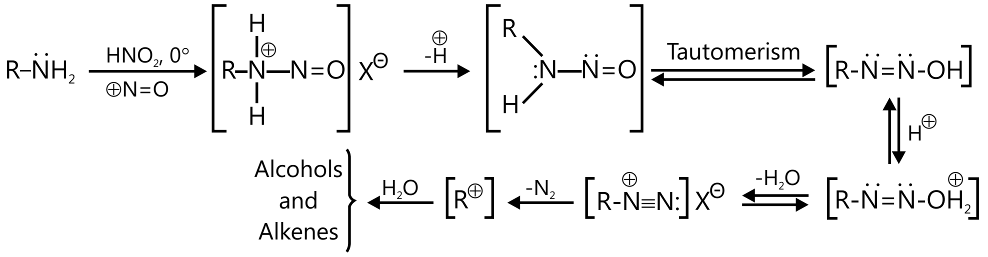
Under the acidic conditions of this reaction, **<u>all amines</u>** undergo reversible salt formation:



$$R^2-\overset{R^1}{\underset{R^3}{N}}: + HX \rightleftharpoons R^2-\overset{R^1}{\underset{R^3}{N}}-\overset{\oplus}{H}\ X^{\ominus}\ [X = HSO_4 \text{ or } NO_2]$$

This happens with 3°-amines, and the salts are usually in water. The reactions of nitrous acid with 1°- and 2°-aliphatic amines may be explained by considering their behaviour with the nitrosonium cation, $NO^{(+)}$, an electrophilic species present in acidic nitrous acid solution.

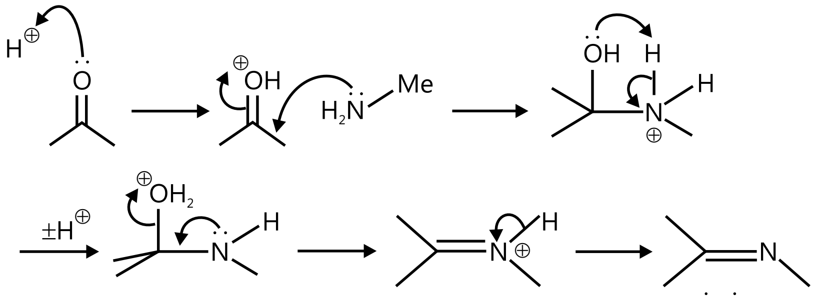
Mechanism of reaction of Nitrous acid with primary amine



6. CHEMICAL REACTIONS OF AMINES

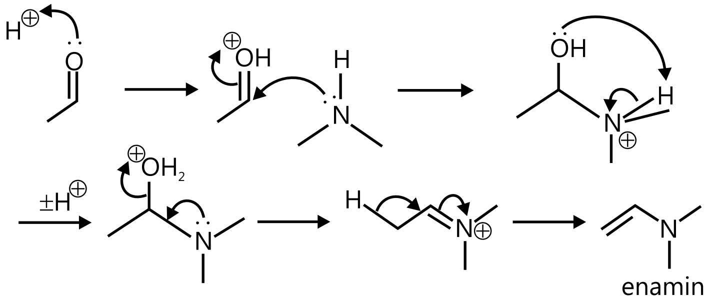
6.1 Reaction with Carbonyl Compounds

(a) Imine Formation



Imines are formed when any primary amine reacts with an aldehyde or ketone under appropriate conditions. Imine formation requires an acid catalyst, otherwise the reaction is very slow. The acid is needed for the elimination of water.

(b) Enamine Formation:



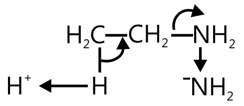
Under the appropriate conditions, secondary amines react with carbonyl compounds to form enamines. Like imine formation, the formation of an enamine also requires an acid catalyst for the removal of water.

6.2 Elimination

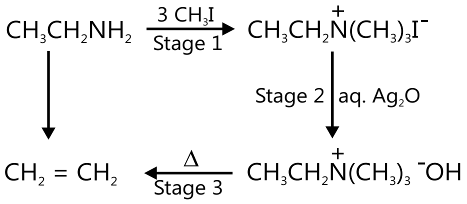
(a) **Hofmann Elimination:** When a primary amine bearing one of more beta hydrogens is treated with methyl iodide, followed by aqueous silver oxide, followed by heat, the primary amine is converted to an alkene. This reaction is known as Hofmann elimination, not to be confused with Hofmann rearrangement.

E.g. $CH_3CH_2NH_2 \xrightarrow[3.\ \Delta]{\substack{1.\ 3\,eq.\,CH_3I \\ 2.\ aq.\,Ag_2O}} CH_2 = CH_2$

The net reaction is 1,2-elimination, hence the name Hofmann Elimination.

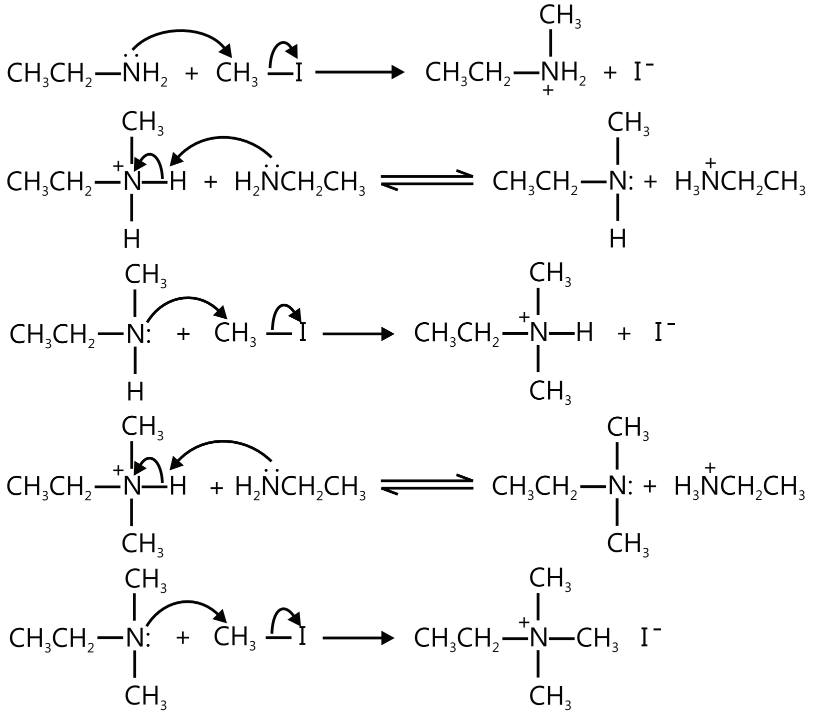


Hofmann elimination occurs in three stages.

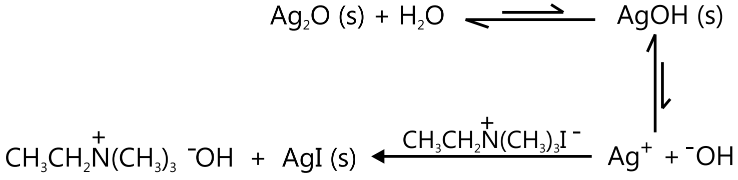


Mechanism:

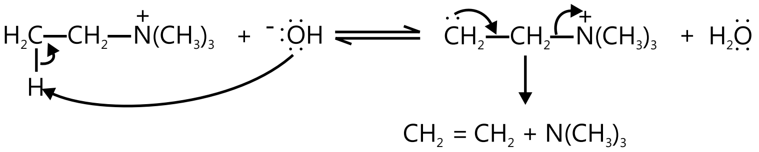
Stage 1:



Stage 2:

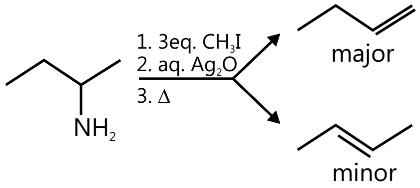


Stage 3:

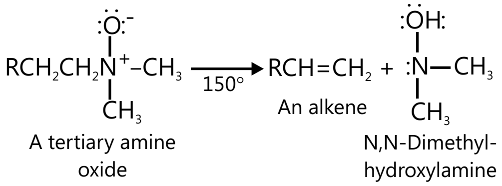


Stage 3 is a 1,2-elimination via E1CB mechanism. Hofmann elimination is regioselective. Since the 1,2-elimination in Stage 3 occurs via E1CB mechanism. Hofmann rule is used to predict the major product.

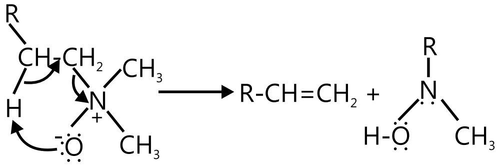
eg.



(b) Cope's Elimination: Tertiary amine oxides undergo the elimination of a dialkylhydroxylamine when they are heated. This reaction is called the Cope elimination:

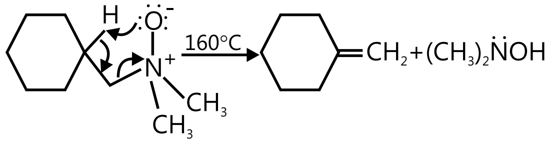


The Cope elimination is a syn elimination and proceeds through a cyclic transition state:

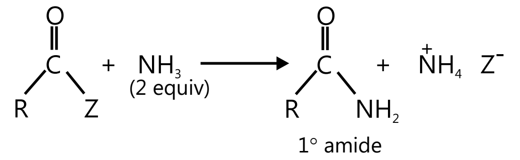


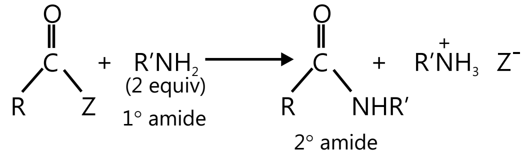
Tertiary amine oxides are easily prepared by treating amines with hydrogen peroxide.

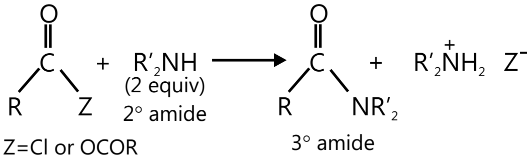
The Cope elimination is useful synthetically. Consider the following synthesis of methylenecyclohexane:



6.3 Reaction with Acid Halides and Anhydrides



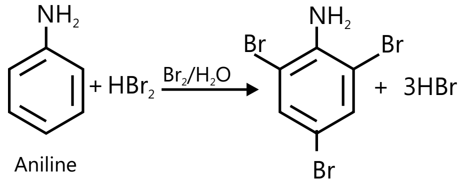




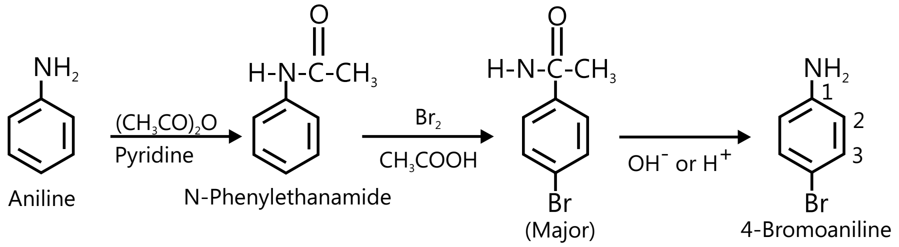
6.4 Electrophilic Substitution Reaction for Aniline

Electrophilic substitution: Due to +M effect of $-NH_2$ generate electron density at ortho and para position hence, aniline active toward electrophilic substitution

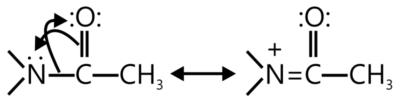
(a) **Bromination:** Aniline reacts with bromine water at room temperature to give a white precipitate of 2,4,6-tribromoaniline.



If we have to prepare a monosubstituted aniline derivative. This can be done by protecting the $-NH_2$ group by acetylation with an acetic anhydride, then carrying out the desired substitution followed by the hydrolysis of the substituted amide to the substituted amine.

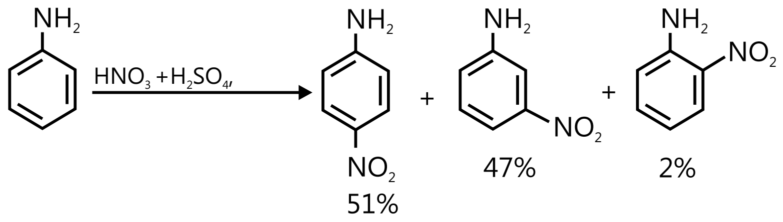


The lone pair of electrons on nitrogen of acetanilide interacts with oxygen atom due to resonance as shown below:

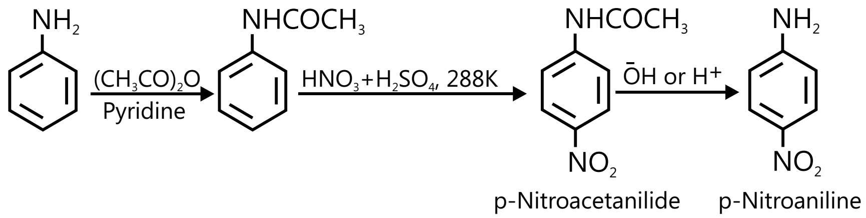


Hence, the lone pair of electrons on nitrogen is less available for donation to the benzene ring by resonance. Therefore, activating the effect of $-NHCOCH_3$ group is less than that of amino group.

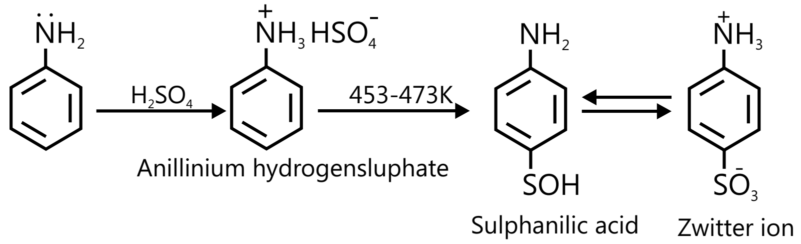
(b) **Nitration:** Direct nitration of aniline is not possible because in the strongly acidic medium, aniline is protonated to form the anilinium ion which is meta directing.



However, by protecting the $-NH_2$ group by acetylation reaction with acetic anhydride, the nitration reaction can be controlled and the p-nitro derivative can be obtained as the major product.



(c) Sulphonation:



PLANCESS CONCEPTS

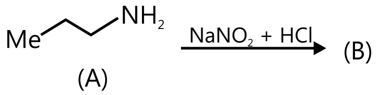
Chemical reaction of amines:

- **Tips and tricks:** Only primary amines react with carbonyl compounds to give imines while secondary amines react with carbonyl compounds to give enamines.
- **Tips and tricks:** In Hoffman elimination, the alkene which is substituted least is the major product while in Cope's elimination the alkene which is most substituted is the major product..
- **Tips and tricks:** In the Hoffmann elimination, there is anti-elimination while in Cope's elimination, there occurs syn elimination.
- In electrophilic substitution of bromine on aniline, if the medium is CS_2 then only 1 Br is substituted while in aqueous solution, the substitution of bromine occurs 3 times.
- If bromination is to be done once in aqueous solution then acetylation of bromine is carried out due to which the ring becomes less activated.
- In nitration, the major products are para and metanitroaniline while the ortho product is very less. This is because of the acid base reaction between aniline and nitrous acid due to which some of aniline becomes meta directing.

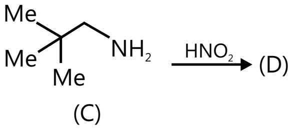
Vaibhav Krishnan (JEE 2009 AIR 22)

Illustration 8: Complete the following reactions: **(JEE MAIN)**

(a)

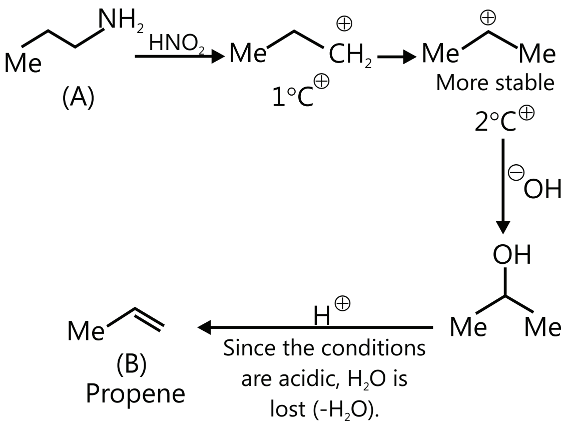


(b)



Sol: Attack of nitrous acid forms a primary carbocation which gets rearranged to more stable secondary carbocation. Attack of nucleophile (OH^-) result in formation of secondary alcohol which on treatment with acid forms alkene.

(a)



(b)

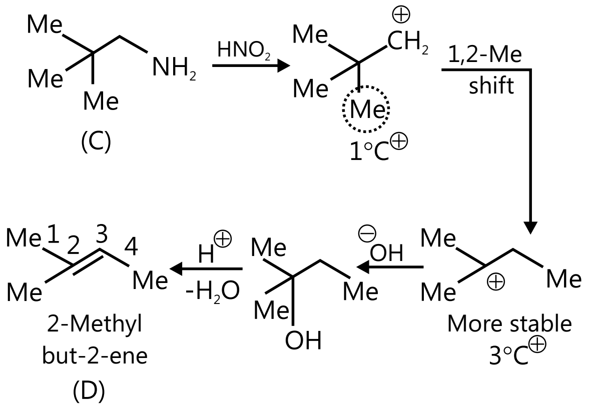
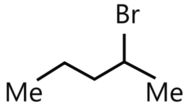
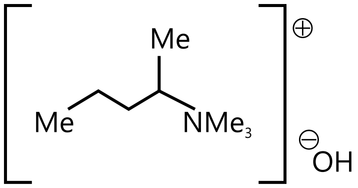


Illustration 9: Explain: **(JEE ADVANCED)**

I. Dehydrohalogenation of

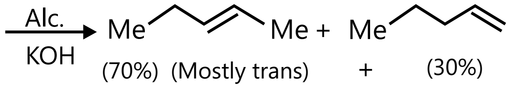


II. Hofmann elimination of



Sol: E2 elimination of an alkyl halide with base $\left(Et\bar{O}\right)$ gives mainly Saytzeff alkene (i.e., more-substituted alkene)

I.



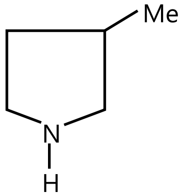
II. $\xrightarrow{\Delta}$ 3% (cis and trans) + (97%)

E2 elimination of an alkyl halide with the base $\left(Et\bar{O}\right)$ gives mainly a Saytzeff alkene (i.e., more-substituted alkene), whereas 4° ammonium salt undergoes Hofmann elimination to give a less-substituted alkene, resulting from a loss of a more acidic β -H (1°>2°>3°) called Hofmann's rule.

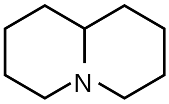
Thus, the acidity of β –H is more important than the stability of the alkene that is formed.

Illustration 10: Give the products of the following by the application of Hofmann's exhaustive methylation and elimination: **(JEE ADVANCED)**

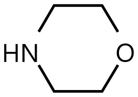
(i)



(ii)

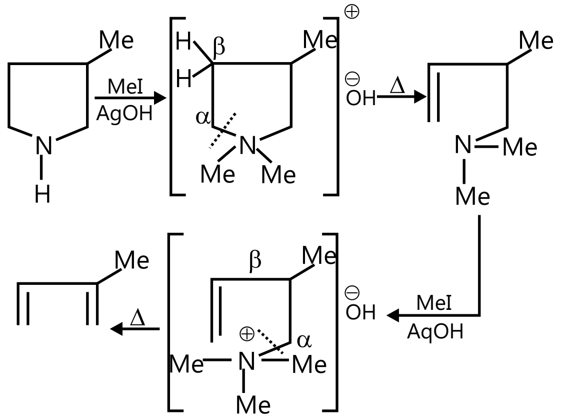


(iii)

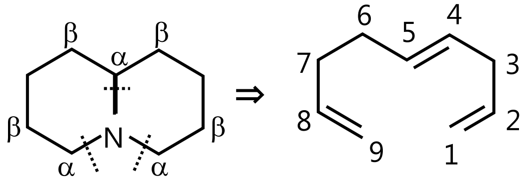


Sol: This process involves thermal decomposition of quaternary ammonium hydroxide compounds to yield an olefin and water is known as Hofmann's exhaustive methylation reaction. This method has been employed in identifying site of unsaturation present in the given compound.

(i)

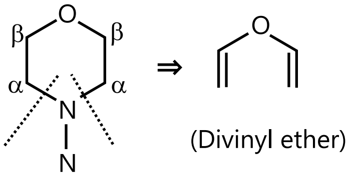


(ii)



(Nona-1,4,8-triene)

(iii)



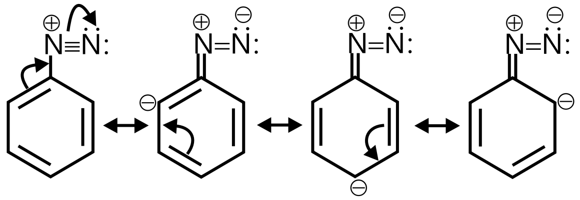
(Divinyl ether)

7. DIAZONIUM SALTS

7.1 Introduction

The diazonium salts have the general formula RN_2X where R stands for an aryl group and X ion may be Cl, Br, HSO_4, BF_3 etc.

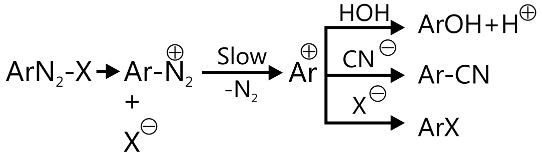
Resonance of benzene diazonium ion is



7.2 Preparation

$$PhNH + NaNO_2 + HCl \xrightarrow{273\text{-}278\ K} \left[Ph\text{-}\overset{\oplus}{N}\equiv N\right]Cl^{\ominus} + NaCl + 2H_2O$$

7.3 Chemical Reactions Involving Displacement of Nitrogen



(a) Replacement by –OH group: $ArN_2Cl + HOH \xrightarrow{\text{Boiling}} ArOH + N_2 + HCl$

(b) Replacement by H: ON reduction with sodium stannite (Na_2SnO_2) (alkaline $SnCl_2$) or hypophosphorous acid (H_3PO_2) or on warming with C_2H_5OH, ArN_2Cl gives benzene.

$ArN_2Cl+H_3PO_2+H_2O \rightarrow ArH+N_2+2CuCl_2$

$ArN_2Cl+Na_2SnO_2+H_2O \rightarrow ArH+N_2+ Na_2SnO_3+HCl$

(c) Sandmeyer reaction (replacement by halogen):

$ArN_2Cl+Cu_2Cl_2+HCl \rightarrow ArCl+N_2+2CuCl_2$

$ArN_2Br+Cu_2Br_2+HBr \rightarrow ArBr+N_2+2CuBr_2$

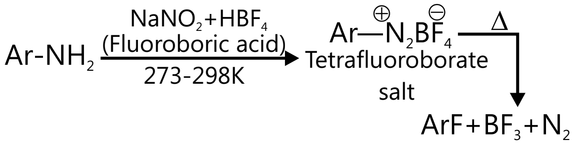
(d) Gattermann reaction:

$ArN_2Cl \xrightarrow{\text{Finely divided Cu/HCl}} ArCl+N_2$

$ArN_2Br \xrightarrow{\text{Finely divided Cu/HBr}} ArBr+N_2$

(e) Iodo compounds: $ArN_2Cl+KI(Aq.) \xrightarrow{\text{Boiling}} Ar\text{–}I +N_2+KCl$

(f) Balz-Schiemann reaction:



(g) Cyano compounds:

$ArN_2Cl+KCN \xrightarrow[\text{or Cu powder}]{\text{CuCN}} ArCN+N_2+KCl$

$ArN_2Cl+KCN \xrightarrow[K_3[Cu(CN)_4]]{} ArCN+N_2+KCl$

(h) Nitro compounds:

$ArN_2Cl+HONO \xrightarrow{Cu_2O} ArNO_2+N_2+HCl$

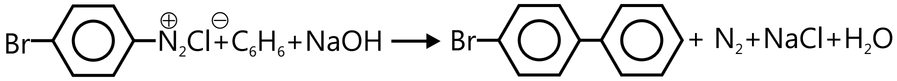
$ArN_2Cl+CuNO_2 \xrightarrow{\Delta} ArNO_2+N_2+CuCl$

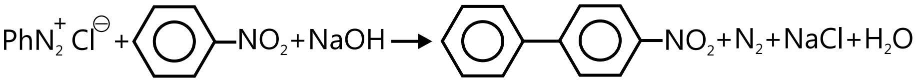
$Ar\overset{\oplus}{N}_2\overset{\ominus}{B}F_4+NaNO_2 \xrightarrow[\text{Cu powder}]{\Delta} Ar\text{–}NO_2+NaBF_4+N_2$

(i) Gomberg reaction (replacement by an aryl group)

$$\underset{\text{Benzene}}{ArN_2Cl+PhH}+NaOH \longrightarrow \underset{\text{Diphenyl}}{Ar\text{–}Ar}+N_2+NaCl+H_2O$$

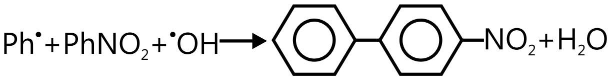
$$\underset{\text{Benzene}}{ArN_2Cl+PhH}+NaOH \longrightarrow \underset{\text{Diphenyl}}{Ar\text{-}Ar}+N_2+NaCl+H_2O$$



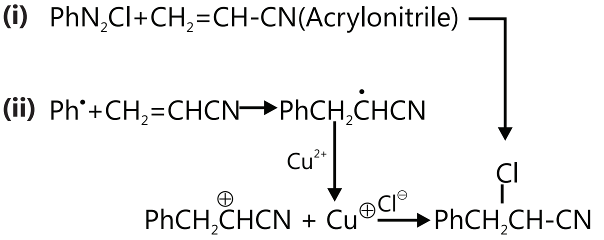


Whatever is the nature of the substituent in the second component, o-and p-substitutions occur and the reaction takes place by the free radical mechanism.

$$Ph\overset{\oplus}{N_2}Cl^{\ominus} \xrightarrow{{}^{\ominus}OH} Ph\text{-}N{=}OH \longrightarrow Ph^{\bullet}+N_2+{}^{\bullet}OH$$



(j) Meerwein Reaction:



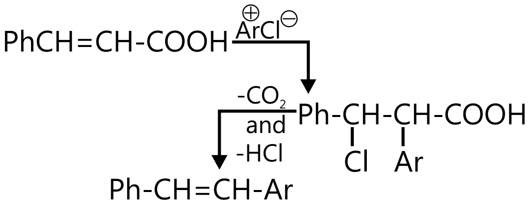
(i) $PhN_2Cl+CH_2{=}CH\text{-}CN(\text{Acrylonitrile})$

(ii) $Ph^{\bullet}+CH_2{=}CHCN \longrightarrow PhCH_2\dot{C}HCN \xrightarrow{Cu^{2+}} PhCH_2\overset{\oplus}{C}HCN + Cu^{\oplus} \xrightarrow{Cl^{\ominus}} PhCH_2\underset{}{\overset{Cl}{\overset{|}{C}}}H\text{-}CN$

(iii) Addition to α, β-unsaturated acid is accompanied by decarboxylation.

$$ArN_2Cl+\underset{\text{Cinammic acid}}{PhCH{=}CH\text{-}COOH} \longrightarrow \underset{\text{(Stilbene)}}{PhCH{=}CH\text{-}Ar}+N_2+CO_2+HCl$$

(iv) Mechanism:



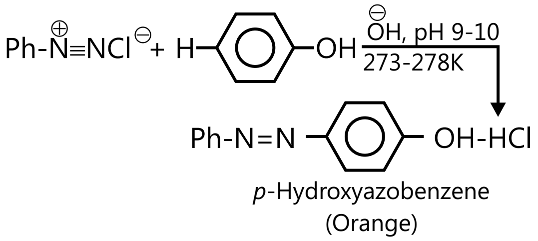
$$PhCH{=}CH\text{-}COOH \xrightarrow{Ar\overset{\oplus}{}Cl^{\ominus}} Ph\text{-}\underset{Cl}{\underset{|}{C}}H\text{-}\underset{Ar}{\underset{|}{C}}H\text{-}COOH \xrightarrow[\text{-HCl}]{\text{-}CO_2\text{ and}} Ph\text{-}CH{=}CH\text{-}Ar$$

Reduction:

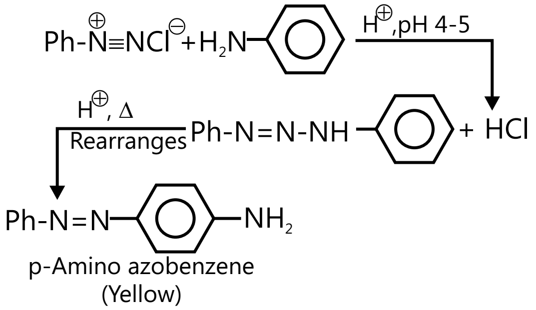
$$Ar\text{–}N{=}N\text{–}Cl \xrightarrow[{[H]}]{Zn+HCl} [Ar\text{–}NH.NH_2] \xrightarrow[{[H]}]{Zn+HCl} Ar\text{–}NH_2+NH_3$$

7.4 Coupling Reactions (Retention of Diazo Group)

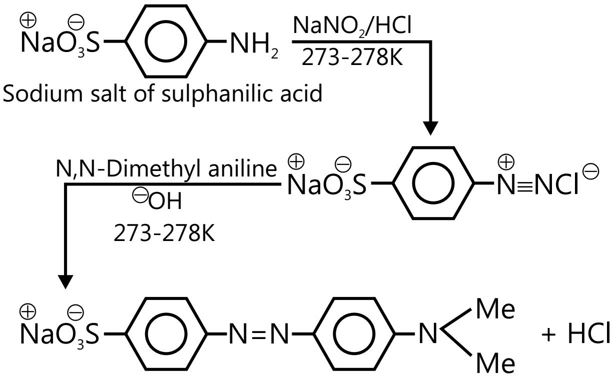
(a)



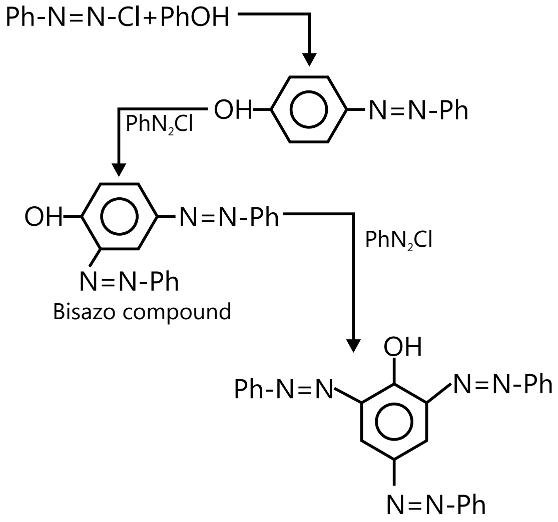
(b)



(c)

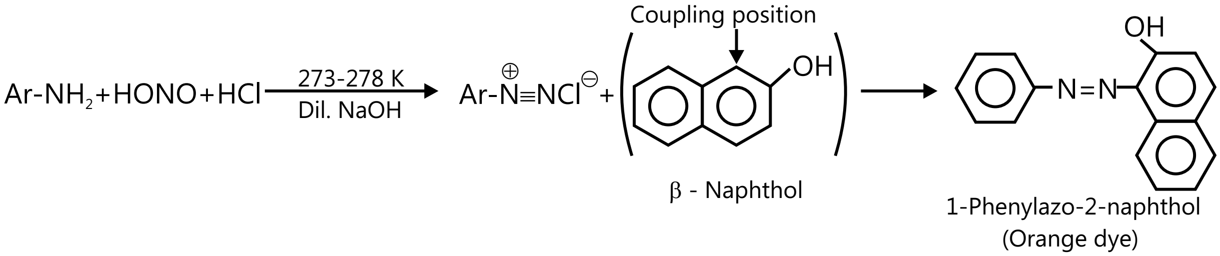


(d) With excess of diazonium salts, the bisazo (o- and p-) and the trisazo compounds may be produced.

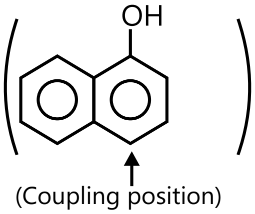


The introduction of a second azo group is facilitated by the presence of an alkyl group in the *para*-position to the hydroxyl group or by two (–OH) groups in the *m*-position.

(e) Dye test (test for 1° aromatic amine):

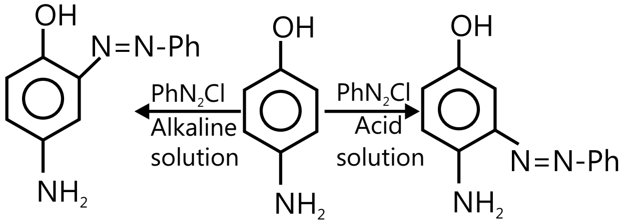


Coupling with α -or 1-naphthol takes places at the position shown by an arrow.

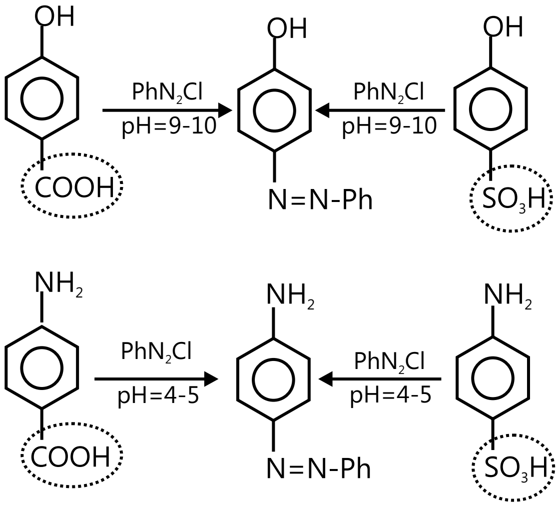


(f) In case, a compound contains both (–OH) and (–NH_2) groups, the coupling takes place at o-position of the amino group in the acid solution.

In the alkaline solution, coupling takes place at *o*-position to the (–OH) group.



(g) In cases where a (–COOH) or (–SO_3H) group is present at p-position to (–OH) or to (–NH_2). it is an example of ipso substitution, special case of electrophilic aromatic substitution where the leaving group is not hydrogen.



PLANCESS CONCEPTS

- Diazonium salts of alkanes, alkenes and alkynes are not at all stable at room temperature while benzene Diazonium salts are stable to some extent due to delocalization of the positive charge in the benzene ring.
- Whenever you see a nucleophile with benzene Diazonium salt, substitute it in place of $N_{2,}$ as it is a very good leaving group.
- Benzene Diazonium salt gives an orange red dye with β-naphthol due to extended conjugation and is hence a test for it.
- Being an electron deficient species benzene Diazonium salt shows a coupling reaction with an electron rich species such as phenol and amines.

Nikhil Khandelwal (JEE 2009 AIR 94)

Illustration 11: Give the decreasing order of the reactivity of the diazonium ion coupling with the phenol.

(JEE MAIN)

(I) $p\text{-}NO_2\text{–}C_6H_4\overset{\oplus}{N}2$ (II) $p\text{-}Cl\text{–}C_6H_4\overset{\oplus}{N}2$ (III) $C_6C_5\overset{\oplus}{N}2$ (IV) $p\text{-}Me\text{–}C_6H_4\overset{\oplus}{N}2$ (V) $p\text{-}MeO\text{–}C_6H_4\overset{\oplus}{N}2$

Sol: The more Electron withdrawing group in diazonium ion, the faster the coupling is.

The more EWG in diazonium ion, the faster the coupling is.

(I) > (II) > (III) > (IV) > (V) (I) $\Rightarrow$ ($p\text{-}NO_2$, –I, and –R), (II) $\Rightarrow$ (p-Cl, –I)

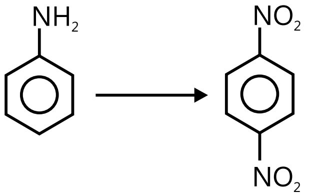
(III) $\Rightarrow$ Standard (IV) $\Rightarrow$ (p-Me, +I, and H.C.)

(V) $\Rightarrow$ [p-MeO–, –I, and + R, net ED power of Me–O is greater than ED power of (Me–) group

Illustration 12: Starting from benzene or toluene or aniline and with the aid of the diazonium salt synthesise the following: p-Nitrobenzene

(JEE MAIN)

Sol: We are going to prepare p-Nitrobenzene from Aniline. Since, $–NH_2$ is o- and p- directing, introduce one ($–NO_2$) group directly by nitration after protecting ($–NH_2$) group (direct nitration of aniline would yield mixture and tarry products).



(a)

Nitration is done using the nitrating mixture (conc.HNO_3+conc.H_2SO_4).Next step is deprotection which is done by using an aqueous base. Now we can introduce the second (NO_2) group via diazonium salt method.

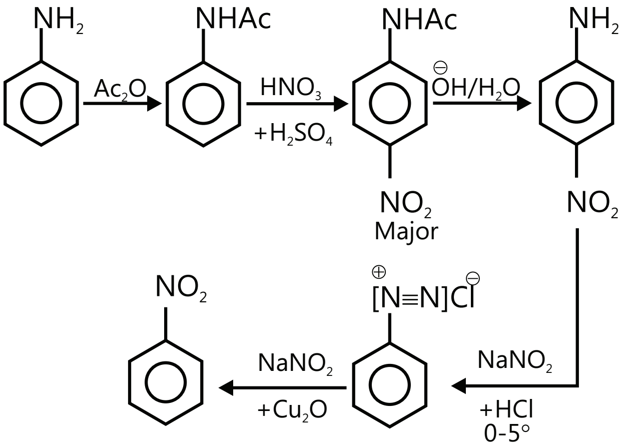


Illustration 13: Explain why 2,4-dinitrobenzene diazonium ion couples with anisole but $PhN_2^{\oplus}$ does not. Write the coupling reaction. **(JEE ADVANCED)**

Sol: The ring is not sufficiently activated by –OMe group for it does not react with most $PhN_2^{\oplus}$ However, $\bar{e}$-withdrawing (–NO_2) groups make this diazonium ion less stable and thus more reactive than $PhN_2^{\oplus}$.

The ring is not sufficiently activated by –OMe group for it does not react with most $PhN_2^{\oplus}$. However, $\bar{e}$-withdrawing (–NO_2) groups make this diazonium ion less stable and thus more reactive than $PhN_2^{\oplus}$.

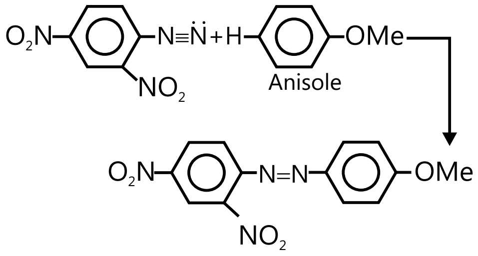
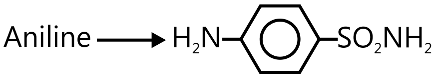
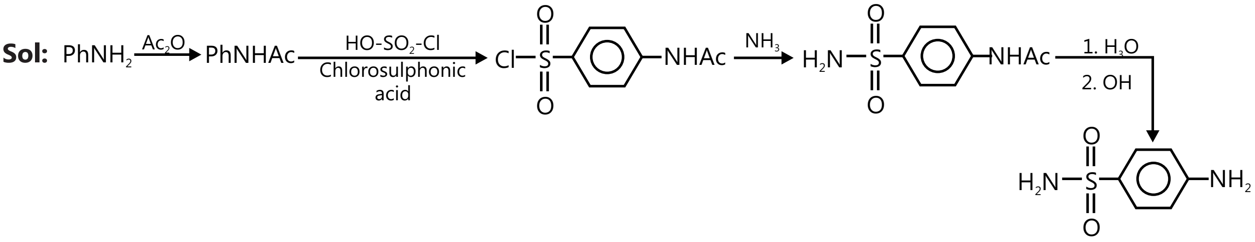


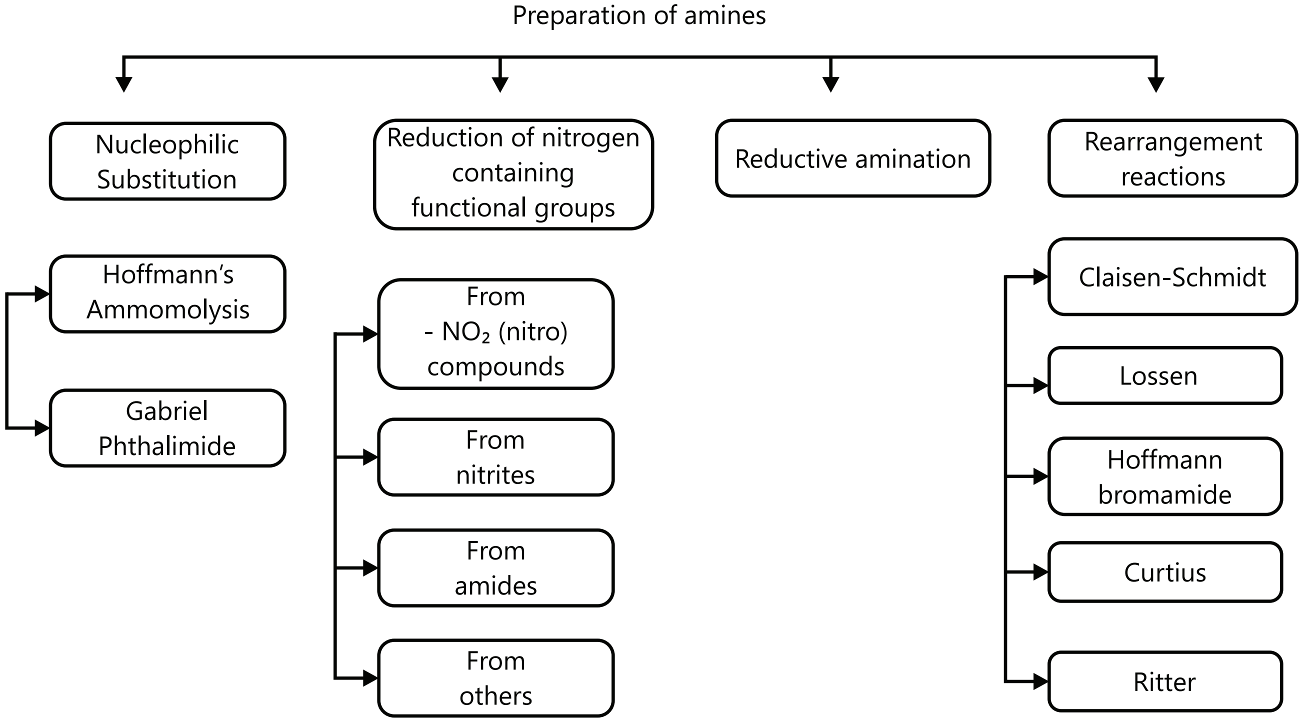
Illustration 14: Convert the following: **(JEE MAIN)**



Sulphanilamide



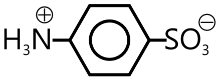
POINTS TO REMEMBER



Solved Examples

JEE Main/Boards

Example 1: Distinguish between the following pairs:

	(I)	(II)
a.	$(PhNH_3)_2^+SO_4^{2-}$	and 
b.	$Me_4N^\ominus Cl^\ominus$	and $\left[Me_3\overset{\oplus}{N}H\right]Cl^\ominus$

Sol: First two compound can be differentiated by using $BaCl_2$ solution as barium will form a ppt with sulphate ion. Other two compound as can be distinguished by treated with NaOH.

a. Add $BaCl_2$ solution. (I) is a sulphate salt and will give a white precipitate of $BaSO_4$. (II) is a sulphonate (sulphonic acid salt) and will not give any precipitate.

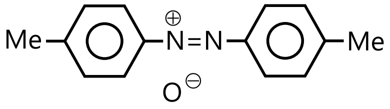
b. Add concentrated NaOH and heat the mixture. (II will change to a volatile free base Me_3N. which has typical NH_3 odour. Compound (I) will not react.

Example 2: Complete the following reactions:

a. $PhNO_2 \xrightarrow{Zn+aq.\,NH_4Cl}$ (I)

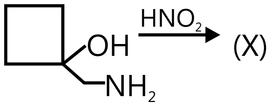
b. $p\text{-}Me–C_6H_4NO_2 \xrightarrow{Al_2O_3/aq.\,NaOH}$ (II)

Sol: a. (I) PhNHOH (N-Phenyl hydroxylamine)

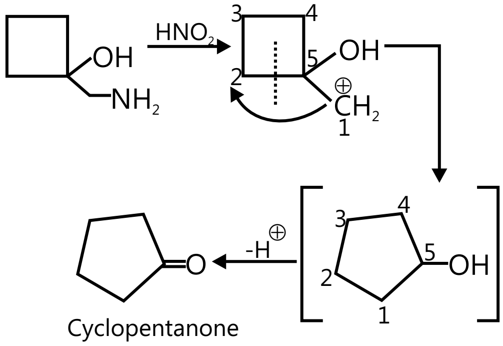
b. (II) 

p-Methyl azoxy benzene

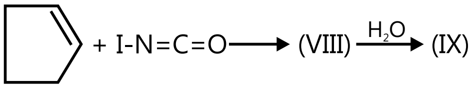
Example 3:



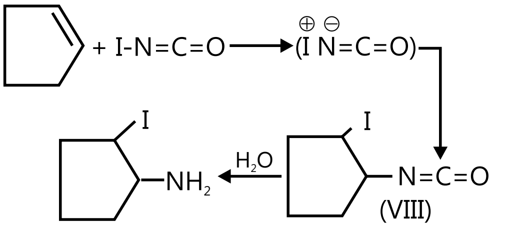
Sol: It is an example of pinacole-pinacolone type ring expansion which takes place via carbocation.



Cyclopentanone
(X)

Example 4: 

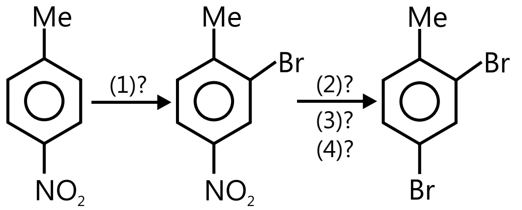
Sol: First step will lead to formation of an isocyanate. On treatment with water it yields primary amine.



(IX)

(VIII)
2-Iodocyclopentyl isocyanate

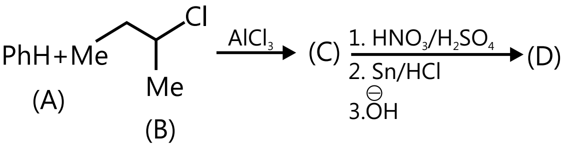
Example 5: Give the reagents in the following reactions:



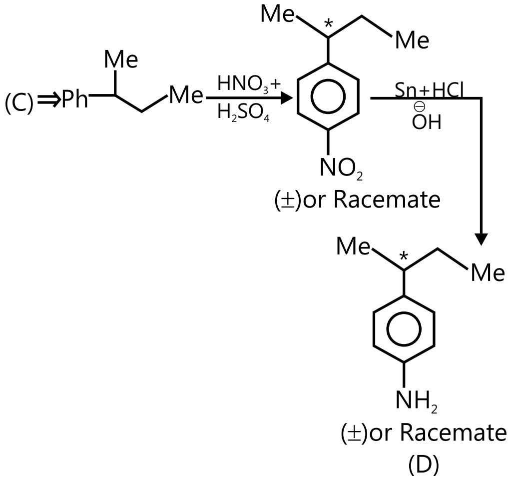
Sol: 1. Br_2 + Fe 2. **Sn + HCl;** $\overset{\ominus}{OH}$

3. **HNO_2 + 0-5°C** 4. **CuBr**

Example 6:

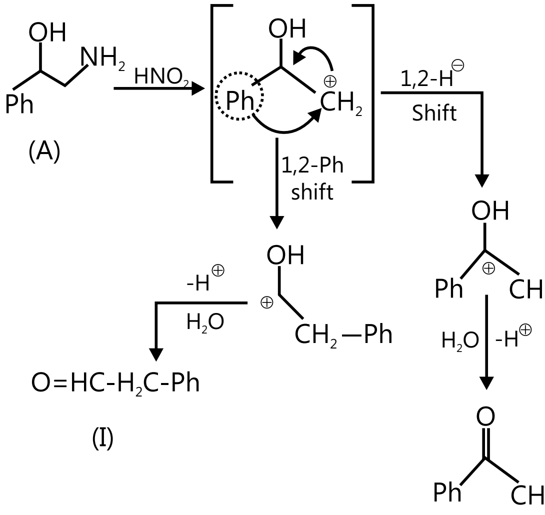


Sol: First step is Friedal craft alkylation. This step produces a new chiral centre on the product but it is optically inactive. The alkylated product is subjected to nitration to introduce nitro group at para position on treatment with reducing agents like Sn+HCl, nitro group gets reduced to amino group.



Example 7: Explain the formation of the mixture $PhCH_2CHO$ (I) and PhCOMe (II) when $PhCH(OH)CH_2NH_2$(A) is treated with HNO_2.

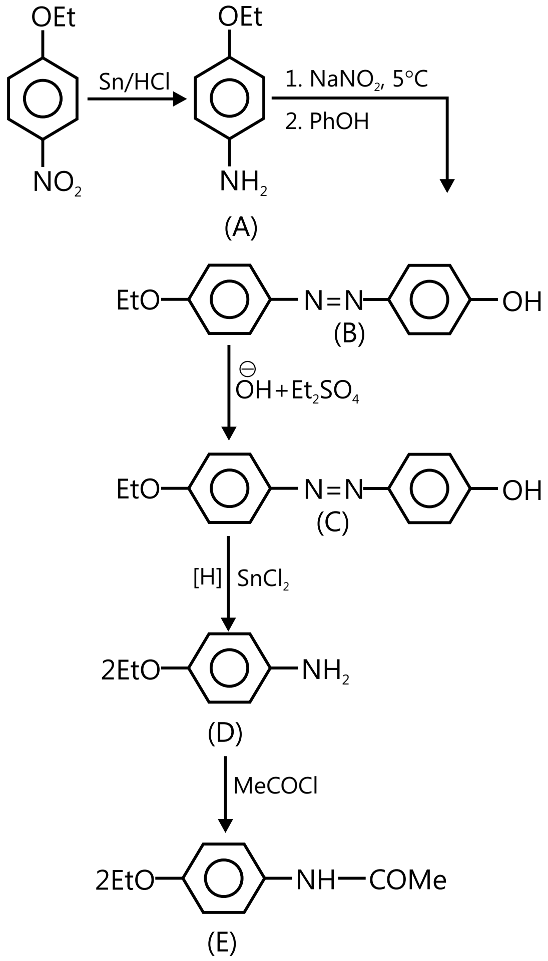
Sol: Attack of Nitrous acid produces primary carbocation which gets rearranged to secondary carbocation and tertiary carbocation. Due to formation of two different carbocation we get different product. With secondary carbocation we end up getting $PhCH_2CHO$ and with tertiary carbocation we get PhCOMe.



Example 8: Identify compounds (A) to (E) in the following:

$$\begin{tikzcd} p\text{-}NO_2C_6H_4OEt \arrow[r, "Sn/HCl"] & (A) \arrow[r, "1.\ HNO_3,\ 5^{\circ}C", "2.\ PhOH"'] & (B) \arrow[d, "\overset{\ominus}{OH}"', "Et_2SO_4"] \\ (E) & (D) \arrow[l, "MeCOCl"'] & (C) \arrow[l, "SnCl_2"'] \\ (C_{10}H_{13}O_2N) & & \end{tikzcd}$$

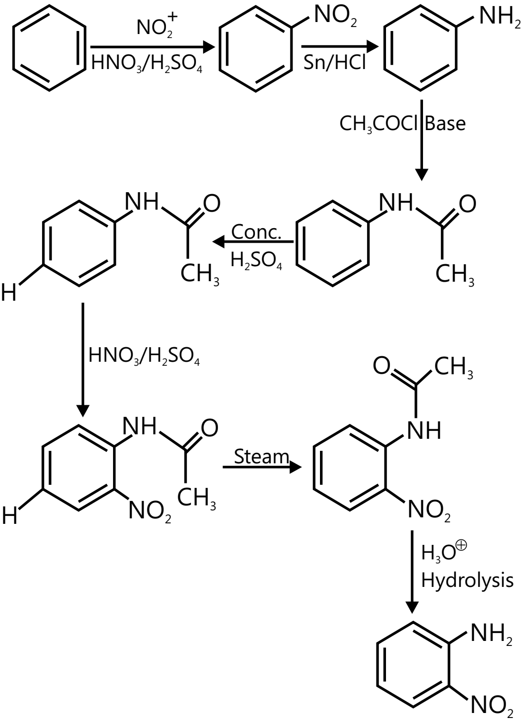
Sol:



Phenacetin
(Analgesic and antiopyretic)

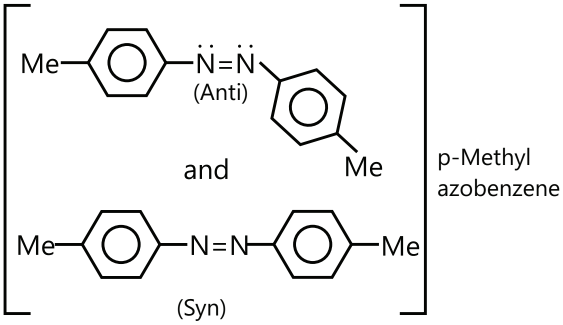
Example 9: Convert benzene to o-nitro aniline as the only product.

Sol:



Example 10: m-Me–$C_6H_4NO_2 \xrightarrow{LAH}$ (III)

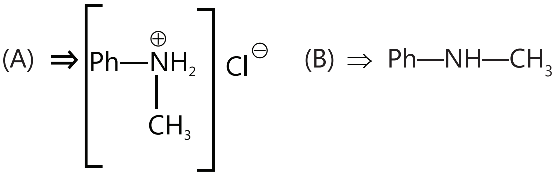
Sol: (III) is



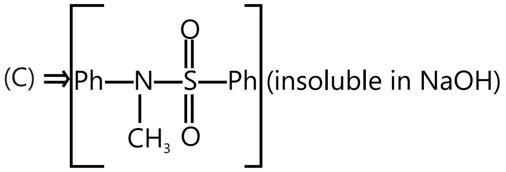
JEE Advanced/Boards

Example 1: The aqueous solution of a nitrogen and chlorine containing organic compound (A) is acidic to litmus. (A) on treatment with aqueous NaOH, it gives a compound (B) containing nitrogen, but not chlorine. Compound (B) on treatment with $C_6H_5SO_2Cl$ in the presence of NaOH gives an insoluble product (C) $C_{13}H_{13}NO_2S$. Give the structures of (A) and (B).

Sol: Quaternary ammonium salt on treatment with aqueous NaOH gives secondary amine. Secondary amine on treatment with benzene sulphonyl chloride its derivative.



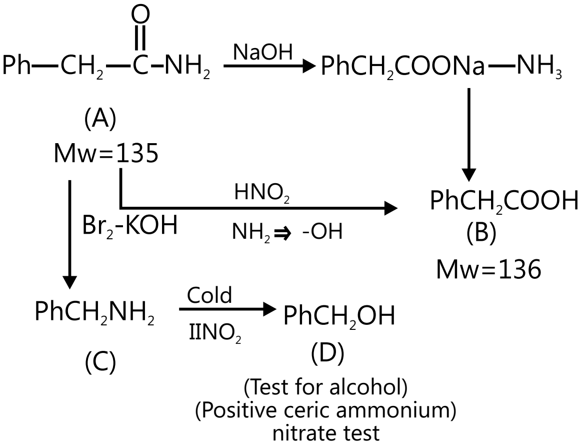
$$(A) \Rightarrow \left[Ph—\overset{\oplus}{N}H_2(CH_3)\right] Cl^\ominus \quad (B) \Rightarrow Ph—NH—CH_3$$

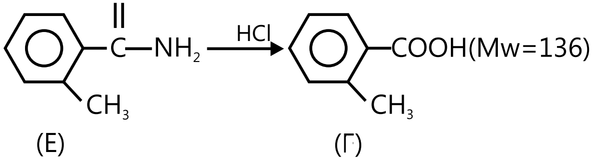


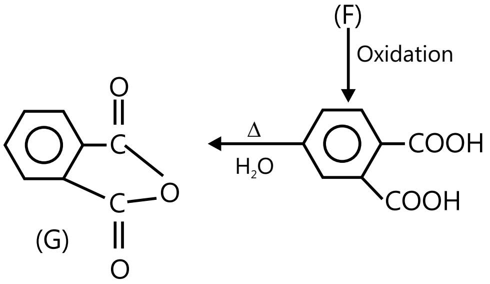
$$(C) \Rightarrow \left[Ph—N(CH_3)—S(=O)_2—Ph\right] \text{(insoluble in NaOH)}$$

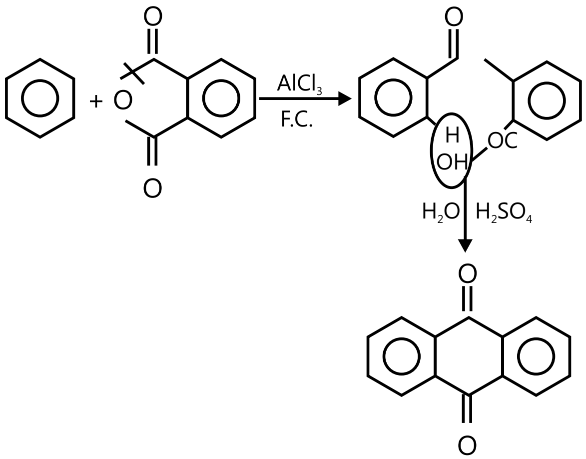
Example 2: An organic compound (A) of molecular weight 135 on boiling with NaOH evolves a gas which gives dense white fumes on bringing a rod dipped in HCl near it. The alkaline solution thus obtained on acidification gives the precipitate of a compound (B), having molecular weight 136. Treatment of (A) with HNO_2 also yields (B), whereas its treatment with Br_2/KOH gives (C). Compound (C) reacts with cold HNO_2 to give (D) which gives 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 $AlCl_3$ to give anthraquinone, Give structures of (A) to (G) with proper reasoning.

Sol:







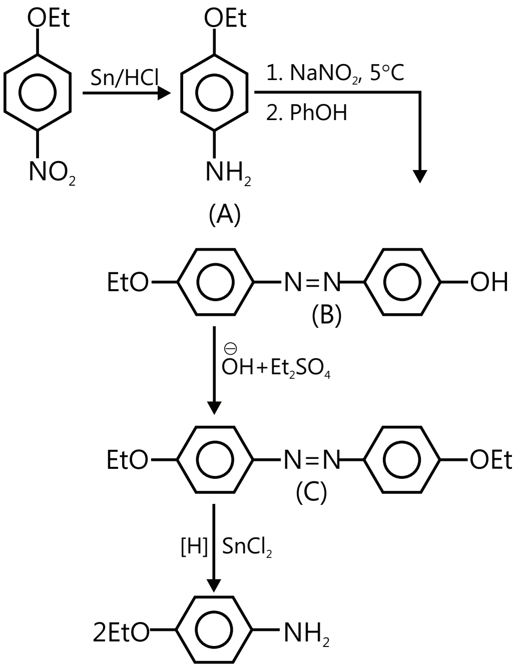


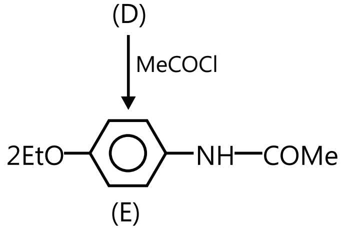
Anthraquinone

Example 3: Identify compounds (A) to (E) in the following:

$$P-NO_2C_6H_4OEt \xrightarrow{Sn/HCl} (A) \xrightarrow[2.PhOH]{1.HNO_2.5^{O}C}$$

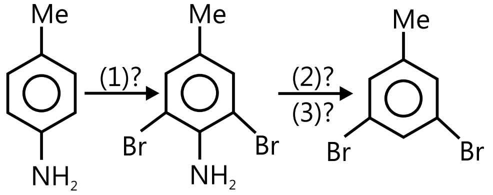
$$(B) \xrightarrow[Et_2SO_4]{\overset{\ominus}{OH}} (C) \xrightarrow{SnCl_2} (D) \xrightarrow{MeCOCl} (E)(C_{10}H_{13}O_2N)$$





Phenacetin
(Analgesic and antipyretic)

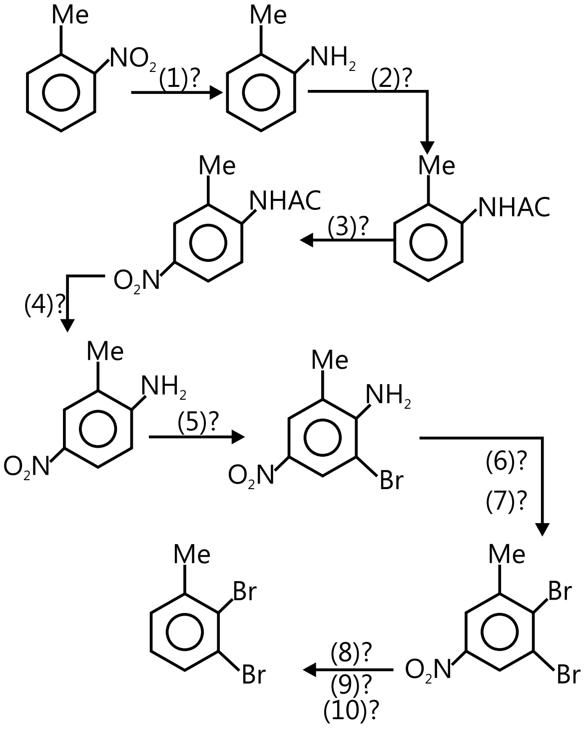
Example 4:



Sol:

1. Br_2 + Fe
2. HNO_2, 0-5°C
3. H_3PO_2

Example 5:



Sol: 1. Sn + HCl   2. Ac_2O

3. HNO_3 + H_2SO_4 4. $\overset{\ominus}{OH}$

5. Br_2 + Fe

6. HNO_2, 0-5°C

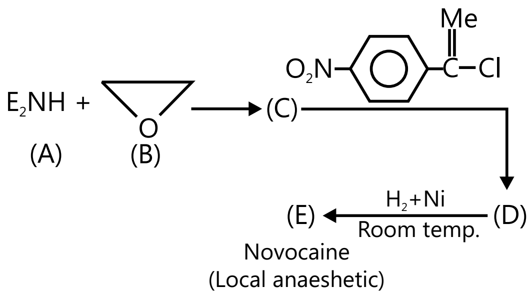
7. CuBr

8. Sn + HCl; $\overset{\ominus}{OH}$

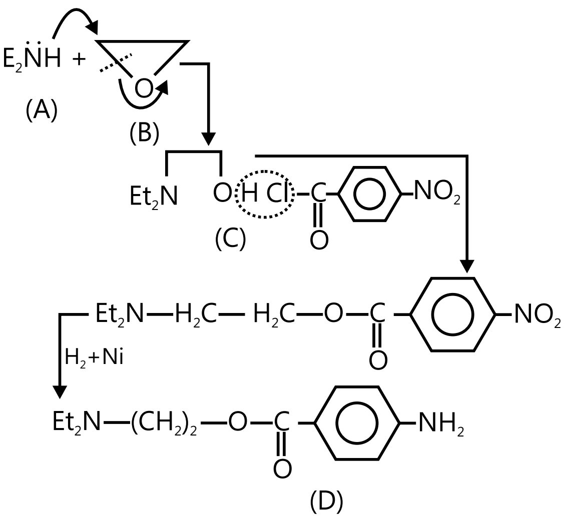
9. HNO_2, 0-5°C

10. H_3PO_2

Example 6:



Sol:



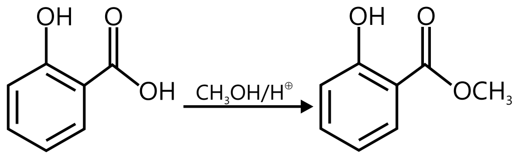
Example 7: A mixture of two organic compounds is added to cold water. After filtration, water-insoluble compound (A) burns with a smoky flame and it does not respond to Lassaigne's and Beilsteins test. When a small amount of this is added to $NaHCO_3$ solution, a colourless gas is evolved with effervescence. When this compound is heated with CH_3OH in acidic medium, it gives the characteristic smell of the oil of wintergreen. Compound (B), which is water soluble, burns with a non-smoky flame and its sodium extract is prepared with cane sugar. It gives a Prussian blue colour with freshly prepared solution of $FeSO_4$ + 2-3 drops NaOH and with few drops of H_2SO_4. When a small amount of this compound is heated in a dry test tube, a colourless gas is evolved that turns moist red litmus paper blue and a white residue is left. This white residue is dissolved in water and a drop of $CuSO_4$ is added in the basic medium-a violet colour is obtained. Identify the compounds (A) and (B) with the help of the reactions involved.

Sol:

i. Compound (A) is insoluble in water and burns with a smoky flame; hence it should be an aromatic compound.

ii. It has no specific element such as N, S and halogens and gives a CO_2 gas with $NaHCO_3$ solution; hence it should contain (–COOH) group.

iii. It gives the oil of wintergreen (methyl salicylate) with CH_3OH in acidic medium; hence it is salicylic acid.



Compound (A)   Methyl salicylate

iv. Compound (B) is water soluble and burns with a non-smoky flame; hence it should be an aliphatic compound.

v. This compound has less carbon content because its sodium extract is prepared with sucrose and it gives a Prussian blue colour with the freshly prepared solution of $FeSO_4$ + 2-3 drops of NaOH and a few drops of H_2SO_4; hence it is a nitrogen-containing compound.

$$NaCN + FeSO_4 \longrightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

$$FeSO_4 \xrightarrow{[O]} Fe_2(SO_4)_3$$

$$3Na_4[Fe(CN)_6] + 3Fe_2(SO_4)_3 \rightarrow \underset{\text{(Prussian blue colour)}}{Fe_4[Fe(CN)_6]_3} + 6Na_2SO_4$$

vi. On heating, it gives ammonia gas, which turns red litmus blue. Hence, it contains (-$CONH_2$) group.

vii. It also gives the biuret test.

$$2NH_2CONH_2 \xrightarrow{\Delta} \underset{\text{Biuret}}{NH_2CONHCONH_2} + NH_3\uparrow$$

$$NH_2CONHCONH_2 \xrightarrow{Cu^{2+}} \text{Violet colour}$$

Hence, this compound is urea (NH_2CONH_2).

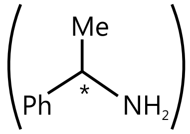
Example 8: Give the structural formula of a chiral compound $C_8H_{11}N$ (X), which dissolves in dilute HCl and evolves N_2 gas with HNO_2.

Sol: D.U. in (X) = $\dfrac{(2n_c + 2) - (n_H - n_N)}{2} = \dfrac{18 - 10}{2} = 4°$

i. 4 D.U. is (X) suggests that is contains benzene ring.

ii. (X) is a 1° amine since it dissolves in HCl and gives N_2 with HNO_2.

iii. The remaining C atom and the NH_2 must form a chiral molecule. So, (X) is:



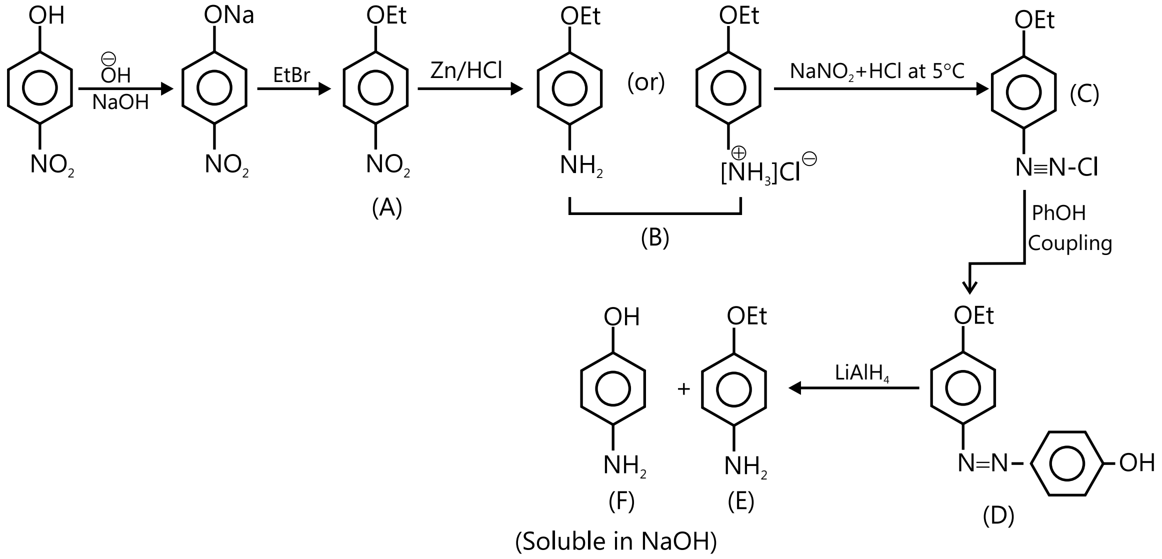
Example 9: Identify compounds (A) through (E) in the following:

$$p\text{-}NO_2C_6H_4OH \xrightarrow[2.\ EtBr]{1.\ \bar{O}H} (A) \xrightarrow{Zn/HCl} (B)$$

$$\xrightarrow[5°C]{NaNO_2/HCl} (C) \xrightarrow{PhOH} (D) \xrightarrow{LiAlH_4} (E)+(F)$$

(F) dissolves in NaOH.

Sol:



JEE Main/Boards

Exercise 1

Q.1 Arrange the following:

(i) In decreasing order of the pK_b values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)NH$ 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) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$,

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

(i) A coupling reaction

(ii) Hofmann's bromamide reaction

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

(ii) 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) Coupling reaction

(ii) Ammonolysis

(iii) Acetylation

(iv) Gabriel phthalimide syntheisis

Q.19 Accomplish the following conversions

(i) Nitobenzene 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) $C_6H_5NH_2 + CHCl_3 + \text{alc. } KOH \rightarrow$

(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 possible 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 How will you convert 4-nitrotoluene to 2-Bromobenzoic acid?

Q.28 Draw the structure of trimethylamine and tell the shape of the molecule. Show the angle between two methyl groups.

Exercise 2

Single Correct Choice Type

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

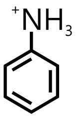
(A) Sulphanilic acid

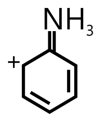
(B) Aniline sulphate

(C) o-aminobenzenesulphonic acid

(D) m-aminobenzenesulphonic acid

Q.2 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.3 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.4 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.5 Which of the following will give a positive carbylamine test?

(A) H_3CNH_2	(B) $H_3C–NH–CH_3$
(C) $(CH_3)_3N$	(D) $C_6H_5NH_2$

Q.6 Isopropylamine can be obtained by

(A) $(CH_3)_2CHO + NH_2OH \rightarrow ? \xrightarrow{LiAlH_4}$

(B) $(CH_3)_2CHO + NH_3 \xrightarrow[\Delta]{} ? \xrightarrow{H_2/Ni}$

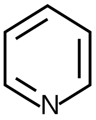
(C) $CHOH + NH_3 \longrightarrow$

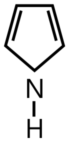
(D) All of these

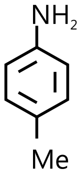
Q.7 The basic strength of amines (ethyl) and ammonia in H_2O is

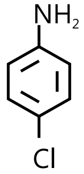
(A) NH_3>p>s>t	(B) P>s>t>NH_3
(C) s>p>t>NH_3	(D) None of these

Q.8 Which of the following will have highest K_b value?

(A)


(B)


(C)


(D)


Q.9 The product not obtained in the following reaction, $CH_3{-}NO_2 + Cl_2 + NaOH \longrightarrow$ is

(A) $ClCH_2NO_2$ (B) Cl_2CHNO_2

(C) Cl_3CNO_2 (D) CH_3NH_2

Q.10 A sequential reaction may be performed as represented below:

$$\text{(a) } R{-}CH_2CO_2H \xrightarrow[(1)]{SO_2Cl_2} R{-}CH_2COCl$$

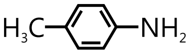
$$\xrightarrow[(2)]{NH_3} R{-}CH_2CONH_2 \xrightarrow[(3)]{} R{-}CH_2NH \xrightarrow[(4)]{}$$

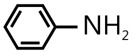
$$R{-}CH_2OH \xrightarrow[(5)]{} R{-}CO_2H$$

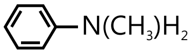
The appropriate reagent for step (3) is

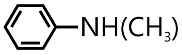
(A) NaBr (B) Bromine+alkali (C) HBr (D) P_2C_5

Q.11 Which of the following amine form N-nitroso derivative when treated with $NaNO_2$ and HCl?

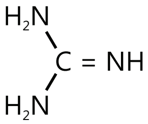
(A)


(B)


(C)


(D)


Q.12 The strongest base among the following is

(A)


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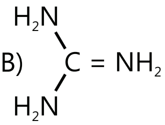
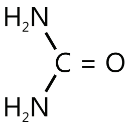
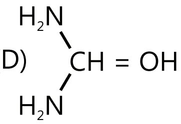
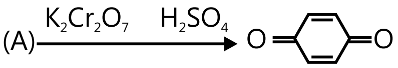
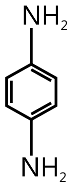


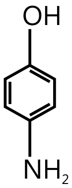
(C)


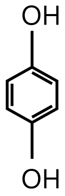
(D)


Q.13 Identify compound (A) in the following oxidation reaction.

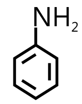


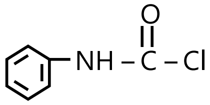
(A)


(B)


(C)


(D) All of these

Q.14

+phosgene ⟶ X. Here X is

(A)


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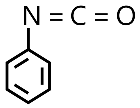

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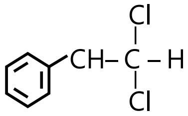


(D) None of these

Q.15 Ethylamine undergoes oxidation in the presence of $KMnO_4$ to give

(A) CH_3COOH (B) CH_3CH_2OH

(C) CH_3CHO (D) N-oxide

Q.16 Baker Mulliken's test is used to detect the presence

(A) –COOH gp (B) $-NO_2$

(C) –OH (D) $-NH_2$

Q.17 t-amines with different alkyl group 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.18 In CH_3NO_2 we can observe

(A) H-bonding

(B) α-halogenation reaction

(C) Tautomerism

(D) All of these

Q.19 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
(i)	Sn and HCl	(p)	Hydrazobenzene
(ii)	Zn and NH_4Cl	(q)	Azoxybenzene
(iii)	Methanolic NaOMe	(r)	Phenyl hydroxylamine
(iv)	Zn and KOH	(s)	Aniline

(A) (i) - q, (ii) - p, (iii) - r, (iv) - s

(B) (i) - s, (ii) - r, (iii) - q, (iv) - p

(C) (i) - p, (ii) - s, (iii) - q, (iv) - r

(D) (i) - p, (ii) - r, (iii) - q, (iv) - s

Q.20 The increasing order of basicity of RCN, RCH=NR and RNH_2 is

(A) $RCN<RCH=NR<RH_2N$

(B) $RNH_2<RCN<RCH=NR$

(C) $RCN>RCH=NR<RNH_2$

(D) None of these

Q.21 How many isomeric amines with that formula C_7H_9N contain a benzene ring?

(A) Two (B) Three (C) Four (D) Five

Previous Years' Questions

Q.1 Match the compounds given in list I with their characteristic reactions given in list II. Select the correct option ***(2010)***

List I	List II
(i) $CH_3CH_2CH_2CH_2NH_2$	(p) Alkaline hydrolysis
(ii) $CH_3C{\equiv}CH$	(q) With KOH (alcohol) and $CHCl_3$ produces bad smell
(iii) $CH_3CH_2COOCH_3$	(r) Gives white ppt. with ammonical $AgNO_3$
(iv) $CH_3CH(OH)CH_3$	(s) With Lucas reagent cloudiness appears after 5 minutes

(A) (i) - q, (ii) - p, (iii) - s, (iv) - r

(B) (i) - r, (ii) - q, (iii) - p, (iv) - s

(C) (i) - q, (ii) - r, (iii) - p, (iv) - s

(D) (i) - s, (ii) - q, (iii) - r, (iv) - p

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

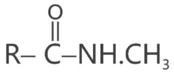
(A) 1 carbon atom less than amide

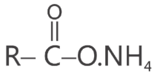
(B) 1 carbon atom more than amide

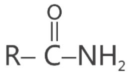
(C) 1 hydrogen atom less than amide

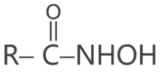
(D) 1 hydrogen atom more than amide

Q.3 Indicate which nitrogen compound amongst the following would undergo Hofmann's reaction (i.e. reaction with Br_2 and strong KOH) to furnish the primary amine ($R{-}NH_2$) ***(1989)***

(A) 
$R{-}\overset{O}{\overset{\|}{C}}{-}NH.CH_3$

(B) 
$R{-}\overset{O}{\overset{\|}{C}}{-}O.NH_4$

(C) 
$R{-}\overset{O}{\overset{\|}{C}}{-}NH_2$

(D) 
$R{-}\overset{O}{\overset{\|}{C}}{-}NHOH$

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

(A) $CH_3NH_2>(CH_3)_3N>(CH_3)_2NH$

(B) $(CH_3)_2NH>CH_3NH_2>(CH_3)_3N$

(C) $CH_3NH_2>(CH_3)_2NH>(CH_3)_2NH$

(D) $(CH_3)_3N>CH_3NH_2>(CH_3)_2NH$

Q.5 The refluxing of $(CH_3)_2NCOCH_3$ with acid gives ***(1996)***

(A) $2CH_3NH_2 + CH_3COOH$

(B) $2CH_3OH + CH_3COOH$

(C) $(CH_3)_2NH + CH_3COOH$

(D) $(CH_3)_2NCOOH + CH_4$

Q.6 Order of basicity of ethyl amines is ***(1988)***

(A) Secondary > Primary > Tertiary

(B) Primary > Secondary > Tertiary

(C) Secondary > Tertiary > Primary

(D) Tertiary > Primary > Secondary

Q.7 The following reaction is RX+KOH (solid) $\xrightarrow{\text{heat}}$ ***(1988)***

(A) Nucleophilic substitution

(B) Electrophilic substitution

(C) Free radical substitution

(D) None of these

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 ***(1999)***

Q.9 Assertion: Amines are basic in nature.

Reason: Presence of lone pair of electron on nitrogen atom. ***(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. ***(2005)***

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

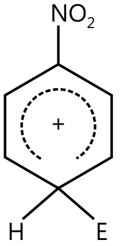
Reason: Nitrogen is less electronegative than oxygen. It is in better position to accommodate the positive charge on the proton. ***(2007)***

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

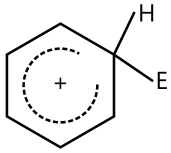
Reason: Fusion of nitrobenzene with solid KOH gives a low yield of a mixture of o- and p- nitro phenols. ***(2008)***

Q.13 The electrophile, E^+ attacks the benzene ring to generate the intermediate σ -complex of the following, which σ-complex is of lowest energy? ***(2008)***

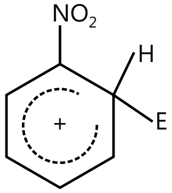
(A)



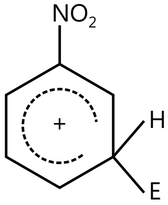
(B)



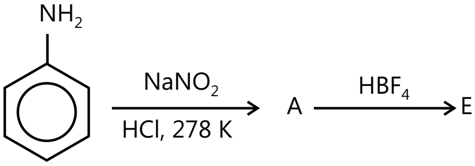
(C)



(D)



Q.14 In the chemical reactions the compounds 'A' and 'B' respectively are ***(2010)***



(A) Nitrobenzene and fluorobenzene

(B) Phenol and benzene

(C) Benzene diazonium chloride and fluorobenzene

(D) Nitrobenzene and chlorobenzene

Q.15 Which of the following compounds can be detected by Molisch's test? ***(2012)***

(A) Nitro compounds (B) Sugars

(C) Amines (D) Primary alcohols

Q.16 On heating an aliphatic primary amine with chloroform and ethanolic potassium hydroxide, the organic compound formed is: ***(2014)***

(A) An alkanol (B) An alkanediol

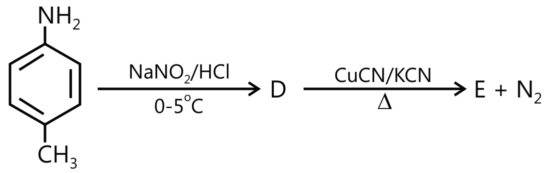
(C) An alkyl cyanide (D) An alkyl isocyanide

Q.17 Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? ***(2014)***

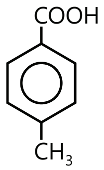
(A) $(CH_3)_2NH$ (B) CH_3NH_2

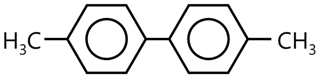
(C) $(CH_3)_3N$ (D) $C_6H_5NH_2$

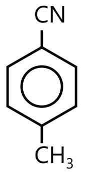
Q.18 In the reaction ***(2015)***

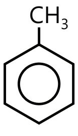


the E is: product

(A) 

(B) 

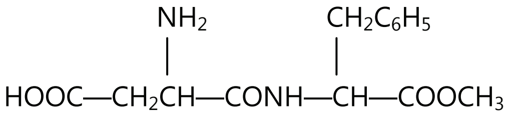
(C) 

(D) 

JEE Advanced/Boards

Exercise 1

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



$$HOOC{-}CH_2\underset{}{\overset{NH_2}{\overset{|}{CH}}}{-}CONH{-}\overset{CH_2C_6H_5}{\overset{|}{CH}}{-}COOCH_3$$

(i) Identify the four functional groups.

(ii) Write the zwitter ionic structure

(iii) Write the structures of the amino acids obtained from the hydrolysis of aspartame.

(iv) Which of the two amino acids is more hydrophobic?

Q.2 Compound of A(molecular formula $C_9H_{11}NO$ 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 0ºC. (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 0–5ºC. What is (A)?

Q.3 An organic compound A, when treated with nitrous acid yields an alcohol B, $C_4H_{10}O$ 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), $C_6H_4N_2O_4$, 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:

(i) Aniline dissolves in aqueous HCl.

(ii) The amino group in ethylamine is basic whereas that in acetamide it is not basic.

(iii) Dimethylamine is a stronger base than trimethylamine.

(iv) Sulphanilic acid although has acidic as well as basic group, it is soluble in alkali but insoluble in mineral acids.

Q.6 Explain, why?

(i) Glycine exists as $H_3N^+CH_2COO^-$ while anthranilic acid, p–NH_2–C_6H_4–COOH does not exist as dipolar ion.

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

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

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

Q.7 Explain with reason?

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

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

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

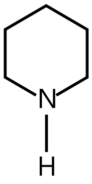
Q.8 Explain it?

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

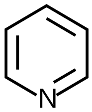
(ii) Tertiary amines do not undergo acetylation. Comment

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

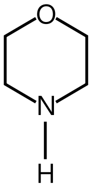
(iv) In the following compounds:



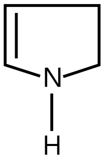
(I)



(II)



(III)



(IV)

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

Q.9 Explain it with reason.

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

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

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

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

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

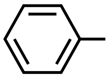
Q.10 Complete the following reactions:

(i) $C_6H_5COOH \xrightarrow{PCl_5} [C] \xrightarrow{NH_3} [D]$

$\xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2/Hi} [E]$

(ii)  $CONH_2 \xrightarrow{P_2O_5} F \xrightarrow[\Delta]{H^+} G$

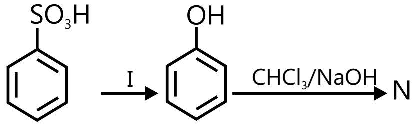
(iii) $EtNH_2 + KCN + Br_2 \xrightarrow{KOH} KBr + H$

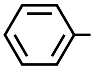
(iv)  $-N(CH_3)_2 + HNO_2 \longrightarrow I$

(v) 2,4-Dinitroaniline $\xrightarrow[\text{(ii) anisole}]{\text{(i) } NaNO_2/HCl,\ 5°C}$ (J)

(vi) $C_6H_6 \xrightarrow{Oleum} (K) \xrightarrow{NaOH} (L)$

$\xrightarrow[heat]{NaOH} (M)$

(vii) 

(viii)  $-SO_3H \xrightarrow[H_2SO_4]{Fuming} O \xrightarrow[\text{(ii)}H^+]{\text{(i)NaOH fuse}} P$

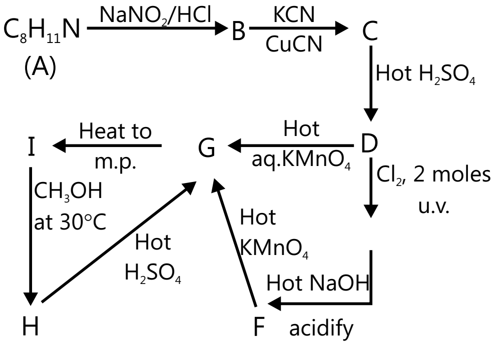
(ix) Phenol $\xrightarrow[NaOH]{Et_2SO_4} (Q) \xrightarrow[AlCl_3]{HCN,\ HCl}$

$(R) \xrightarrow{PhNH.NH_2} (S)$

(x) $CH_3CONHC_6H_5 \xrightarrow{Br_2,\ Fe} T + U$

(xi) $C_6H_5N_2Cl \xrightarrow{(A)} (V)$ Gattermann reaction

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 nitrogen, but not chlorine. Compound (B) on treatment with $C_6H_5SO_2Cl$ in the presence of NaOH gives an insoluble product (C), $C_{13}H_{13}NO_2S$. 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 Na/C_2H_5OH 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 when cyclopentanone reacts with

(i) $CH_3CH_2NH_2$ (1° amine)

(ii) $(CH_3CH_2)_2NH$ (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 C_3H_7NO. 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 $C_7H_7NO_2$ dissolves in $NaHCO_3$ to evolve CO_2 and when reacted with $NaNO_2/HCl$ forms (b), $C_7H_6O_3$. (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), $C_6H_3N_3O_7$. (C) undergoes acetylation and decomposes $NaHCO_3$ to evolve CO_2. On reaction with PCl_5 (C) is converted to (D), $C_6H_5N_3O_6Cl$ which when reacted with water gives back (C). Identify compounds (A) to (D).

Q.24 Compound (A) having M.F. C_8H_8O on treatment with $NH_2OH.HCl$ 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 C_8H_9NO. When (D) is boiled with alcoholic KOH, and oil (F) C_6H_7N 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), $C_7H_6O_2$. Identify the compounds (A) to (G).

Q.25 An aromatic compound (A), having M.F $C_7H_5NO_2Cl_2$ 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 C_7H_9N on treatment with $NaNO_2$ and HCl at room temperature forms another compound (B), C_7H_8O. 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_7N. 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°C, an ionic compound (C) $C_7H_7N_2Cl$ is obtained. (C) yields a red dye with alkaline β-napththol 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

Single Correct Choice Type

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	List II
(i) Propyne	(p) Reduces Fehling's solution
(ii) Ethyl benzoate	(q) Forms a precipitate with $AgNO_3$+C_2H_5OH
(iii) Acetaldehyde	(r) Insoluble in water, but dissolves in aqueous NaOH upon heating
(iv) Aniline	(s) Dissolves in dil. HCl in the cold and is reprecipitated by the addition of alkali

(A) (i) - r, (ii) - q, (iii) - p, (iv) - s

(B) (i) - q, (ii) - r, (iii) - p, (iv) - s

(C) (i) - q, (ii) - r, (iii) - s, (iv) - p

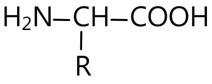
(D) (i) - p, (ii) - r, (iii) - q, (iv) - s

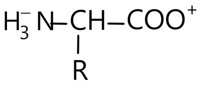
Q.2 Activation of benzene ring by $-NH_2$ in aniline can be reduced by treating with

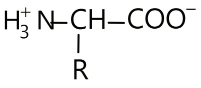
(A) Dilute HCl (B) Ethyl alcohol

(C) Acetic acid (D) Acetyl chloride

Q.3 Dipolar ion structure for amino acid is

(A) 
$H_2N-\underset{\underset{R}{|}}{CH}-COOH$

(B) 
$H_3^{-}N-\underset{\underset{R}{|}}{CH}-COO^{+}$

(C) 
$H_3^{+}N-\underset{\underset{R}{|}}{CH}-COO^{-}$

(D) None of these

Q.4 $-NH_2$ group shows acidic nature while reacts with regent.

(A) Na (B) CS_2 (C) Br_2+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

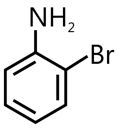
(A) All have same chemical property

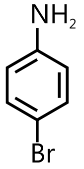
(B) All have one common chemical behaviour

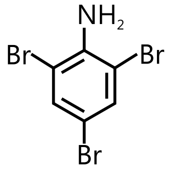
(C) All are basic

(D) None of these

Q.9 Bromine in CS_2 reacts with aniline to give

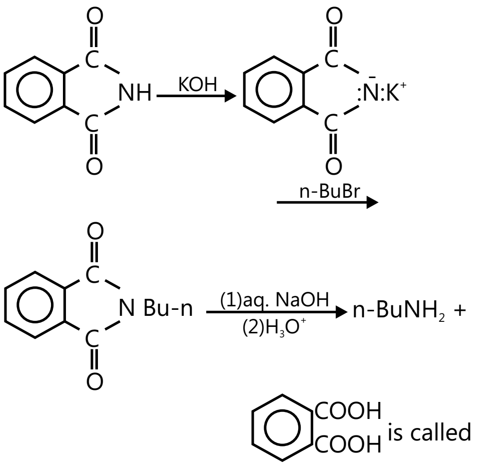
(A) 

(B) 

(C) 

(D) Both (A) and (B)

Q.10 The reaction:



is called

(A) Carbylamine reaction

(B) Hofmann reaction

(C) Gabriel phthalimide synthesis

(D) Cope reaction

Q.11 The conjugate acid of $HO(CH_2)_3NH_2$ is

(A) $H_2\overset{+}{O}(CH_3)_3NH_2$ (B) $HO(CH_2)_3\overset{+}{N}H_3$

(C) $\overset{-}{O}(CH_2)_3NH_2$ (D) $HO(CH_2)_3\overset{+}{N}H$

Q.12 Consider the following compounds:

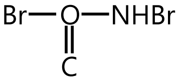
1. $H_2C=CHCH_2NH_2$
2. $CH_3CH_2CH_2NH_2$
3. $HC\equiv CCH_2NH_2$

The increasing order of basicity is

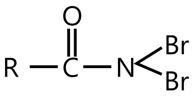
(A) 3<1<2 (B) 3<2<1

(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) 
$Br-\underset{\underset{C}{\|}}{O}-NHBr$

(B) R–NHBr

(C) 
$R-\overset{\overset{O}{\|}}{C}-NBr_2$

(D) R–C=N=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) Methylamine (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.

Multiple Correct Choice Type

Q.19 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.

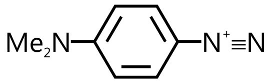
(D) Easier loss of H^+ to regain aromaticity from the meta position than from the ortho and para positions.

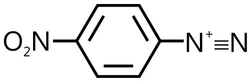
Comprehension Type

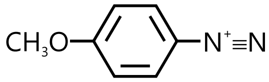
Arene diazonium salts are more stable than alkanediazonium salts due to dispersal of the positive charge on the benzene ring. Obviously electron donating groups favour diazotisation by retarding the decomposition of diazonium salts to phenyl cation. The high reactively of arenediazonium salts is due 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, CH_3CH_2OH, $NaBH_4$ 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.

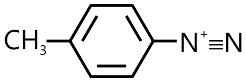
Diazonium salts also couple with phenols and aromatic amines to form coloured azo dyes. The reactivity of diazonium salts towards coupling reactions is favoured by presence of electron withdrawing groups; the reactivity of 2,4,6-trinitrobenzenediazonium chloride is so high that it even couples with reactive hydrocarbons such as mesitylene.

Q.20 Consider the following ions:

(A) 

(B) 

(C) 

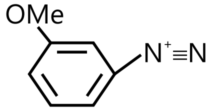
(D) 

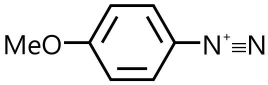
The reactivity of these ions towards azo coupling reactions under similar conditions is

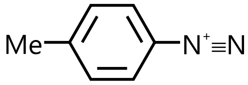
(A) I<IV<II<III (B) I<III<IV<II

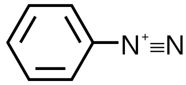
(C) III<I<II<IV (D) III<I<IV<II

Q.21 Which of the following diazonium salts when boiled with dil. H_2SO_4 gives the corresponding phenol most readily?

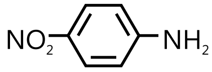
(A) 

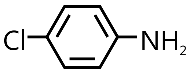
(B) 

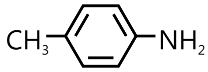
(C) 

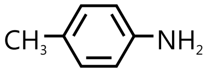
(D) 

Q.22 Which of the following arylamines undergoes diazotisation most readily?

(A) 

(B) 

(C) 

(D) 

Q.23 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

Assertion Reasoning Type

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 assertion and reason true and reason is the correct explanation of assertion, then mark (A)

(B) If both assertion and reason are true but reason is not the correct explanation of assertion, then mark (B)

(C) If assertion is true but reason is false, then mark (C)

(D) If both assertion and reason false, then mark (D)

Q.24 Assertion: Benzyl amine is more basic than aniline.

Reason: Positive inductive effect of phenyl group creates high electron density around N atom.

Q.25 Assertion: White precipitate of silver chloride gets dissolved in NH_4OH solution.

Reason: NH_3 reacts with AgCl to form a solution complex with formula $[Ag(NH_3)_2]Cl$.

Q.26 Assertion: o-nitrophenol is more acidic than p-nitrophenol.

Reason: Nitro group has +M and –I effect.

Q.27 Assertion: 3°amine is proved to be less basic in aq. solution

Reason: Conjugate acid of 3°amine is poorly solvated in aq. solution.

Q.28 Assertion: In order to convert R–Cl to pure R–NH, Gabriel-phthalimide synthesis can be used.

Reason: With proper choice for alkyl halides, phthalimide synthesis can be used to prepare 1°, 2° and 3° amines.

Q.29 Assertion: 4-Nitrochlorobenzene undergoes nucleophilic substitution more readily than chlorobenzene.

Reason: Chlorobenzene undergoes nucleophilic substitution by elimination-addition mechanism while 4-nitrochlorobenzene undergoes nucleophilic substitution by addition-elimination mechanism.

Q.30 Assertion: 1° amides react with Br_2 + NaOH to give 1° amines with one carbon atom less than the parent amide.

Reason: The reaction occurs through intermediate formation of acylnitrene.

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

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

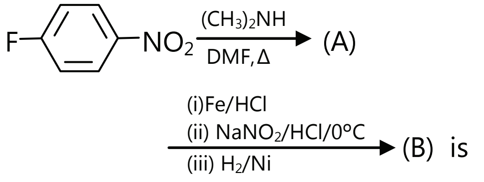
Previous Years Questions

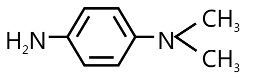
Q.1 Benzene diazonium chloride on reaction with phenol in weakly basic medium gives ***(1998)***

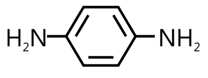
(A) Diphenyl ether (B) p-hydroxy azobenzene

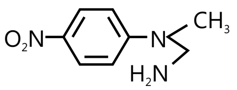
(C) Chlorobenzene (D) Benzene

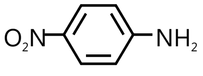
Q.2 ***(2007)***



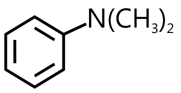
(A)


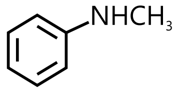
(B)


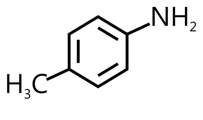
(C)


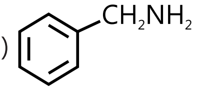
(D)


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)


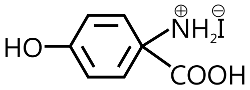
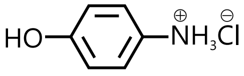
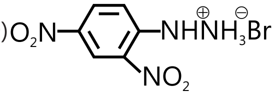
(B)


(C)


(D)


Q.4 Match the Columns

Match the compounds in column I with their characteristic test(s)/reaction(s) given in column II. ***(2010)***

Column I	Column II
(A) $H_2N-\overset{\oplus}{N}H_3\overset{\ominus}{Cl}$	(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.

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

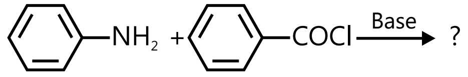
Q.6 The high melting point and insolubility in organic solvents of sulphanilic acid are due to its .... structure. ***(1994)***

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

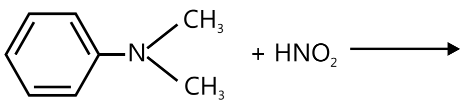
Q.8 State the conditions under which the following preparation carried out.

"Aniline from benzene" ***(1983)***

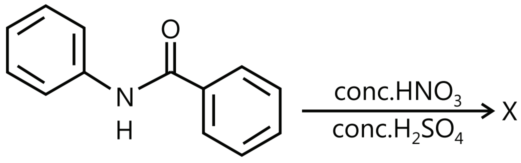
Q.9 Complete the following with appropriate structures: ***(1986)***

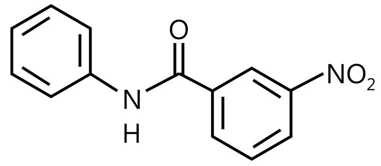


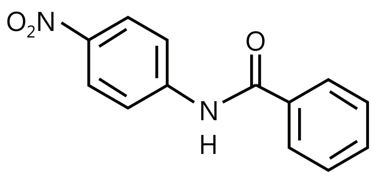
Q.10 Write the structure of the major organic product expected from the following reaction. ***(1992)***

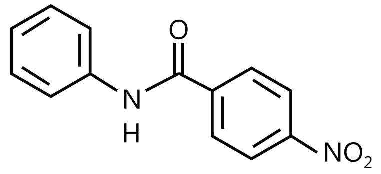


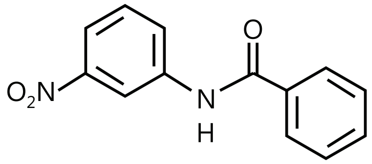
Q.11 In the following reaction the structure of the major product 'X' is: ***(2007)***



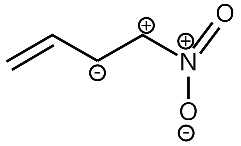
(A) 

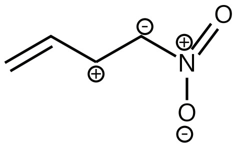
(B) 

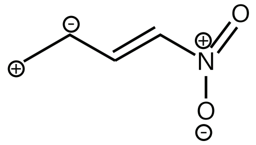
(C) 

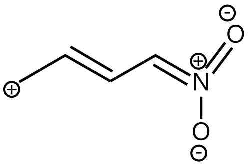
(D) 

Q.12 Among the following, the least stable resonance structure is ***(2007)***

(A) 

(B) 

(C) 

(D) 

Q.13 Statement-I: Aniline on reaction with $NaNO_2/HCl$ at 0°C followed by coupling with β- naphthol gives a dark blue coloured precipitate.

Statement-II: The colour of the compound formed in the reaction of aniline with $NaNO_2/HCl$ at 0°C followed by coupling with β-naphthol is due to the extended conjugation. ***(2008)***

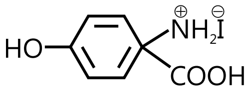
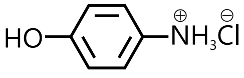
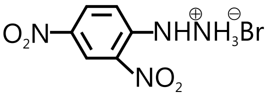
(A) Statement-I-I is True, statement-II is True; statement-II is correct explanation for statement-I

(B) Statement-I is True, statement-II is True; statement-IIis NOT a correct explanation for statement-I

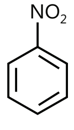
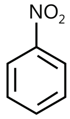
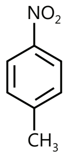
(C) Statement-I is True, statement-II is False

(D) Statement-I is False, statement-II is True

Q.14 Match the compounds in column I with their characteristic test(s)/ reaction(s) given in column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix gives in the ORS ***(2008)***

Column I	Column II
(A) $H_2N-\overset{+}{N}H_3\overset{-}{Cl}$	(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

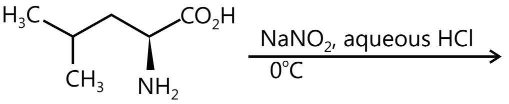
Q.15 Match the four starting materials (P, Q, R, S) given in list I with the corresponding reaction schemes (I, II, III, IV) provided in list II and select the correct answer using the code given below the lists. ***(2014)***

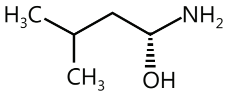
List I	List II
(i) H≡H	(p) Scheme I $? \xrightarrow[\text{(ii) SOCl}_2\text{ (iv) NH}_3]{\text{(i) KMnO}_4\text{, HO}^-\text{, heat (ii), H}_2\text{O}} C_7H_6N_2O_3$
(ii) 	(q) Scheme II $? \xrightarrow[\text{(ii) NHO}_3\text{ (v) dil.H}_2\text{ SO}_4\text{, heat (vi) HO}^-]{\text{(i) Sn/HCl (ii) CH}_3\text{COCl (ii) conc H}_2\text{SO}_4} C_6H_6N_2O_2$
(iii) 	(r) Scheme III $? \xrightarrow[\text{(ii) H}_2\text{S.NH}_3\text{ (iv) NaNO}_2\text{,H}_2\text{SO}_4\text{ (v)hydrolysis}]{\text{(i) red hot iron, 873(ii) fu mingHNO}_3\text{,H}_2\text{SO}_4\text{, heat}} C_6H_5NO_3$
(iv) 	(s) Scheme IV $? \xrightarrow[\text{(ii) conc. HNO}_3\text{, conc. H}_2\text{SO}_4\text{ (iii)dil. H}_2\text{SO}_4\text{. heat}]{\text{(i) conc. H}_2\text{SO}_4\text{, 60}^\circ\text{C}} C_6H_5NO_4$

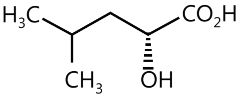
Code:

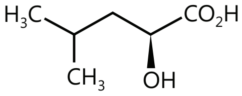
	(i)	(ii)	(iii)	(iv)
(A)	p	s	q	r
(B)	r	p	s	q
(C)	r	s	q	p
(D)	s	p	r	q

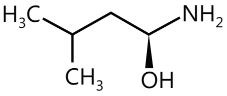
Q.16 The major product of the reaction is ***(2015)***



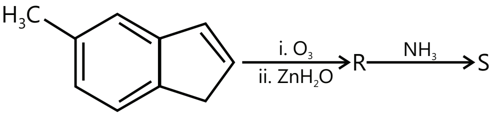
(A) 

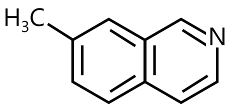
(B) 

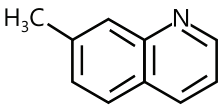
(C) 

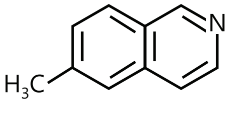
(D) 

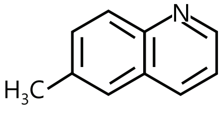
Q.17 In the following reactions, the product S is ***(2015)***



(A) 

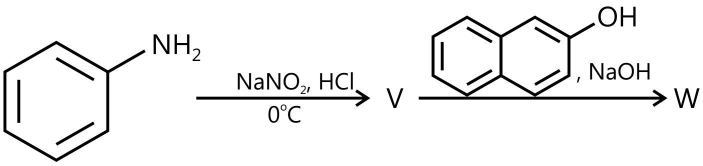
(B) 

(C) 

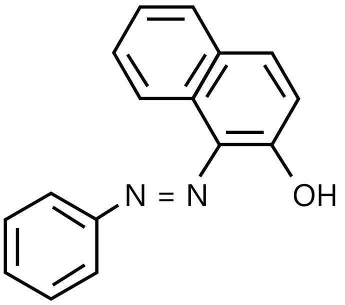
(D) 

Q.18 In the following reactions, the major product W is

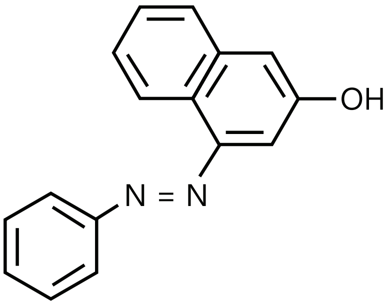
(2015)



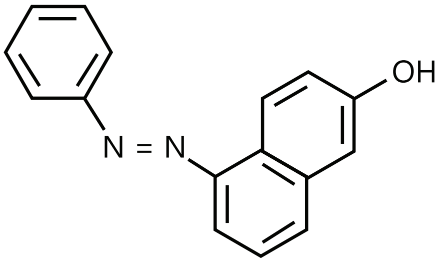
(A)



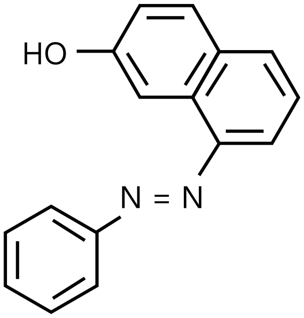
(B)



(C)

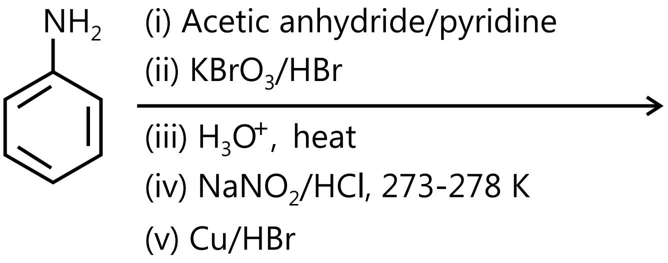


(D)



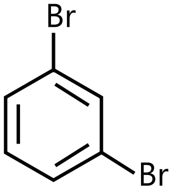
Q.19 The product (s) of the following reaction sequence is (are)

(2016)

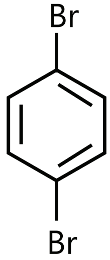


(i) Acetic anhydride/pyridine
(ii) KBrO$_3$/HBr
(iii) H$_3$O$^+$, heat
(iv) NaNO$_2$/HCl, 273-278 K
(v) Cu/HBr

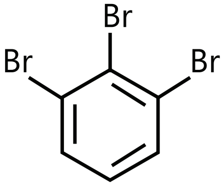
(A)



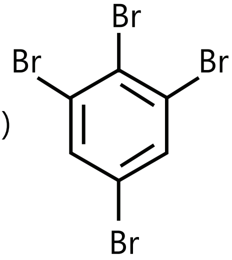
(B)



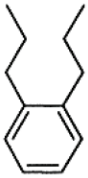
(C)



(D)

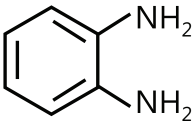


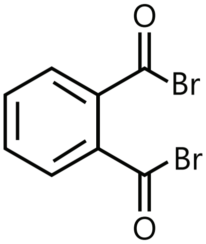
Paragraph: Treatment of compound O with $KMnO_4/H^+$ gave P, which on heating with ammonia gave Q. The compound Q on treatment with Br_2/NaOH produced R. On strong heating, Q gave S, which on further treatment with ethyl 2-bromopropanoate in the presence of KOH followed by acidification, gave a compound T

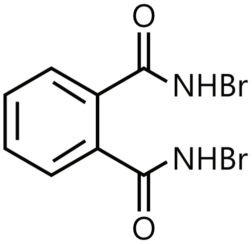


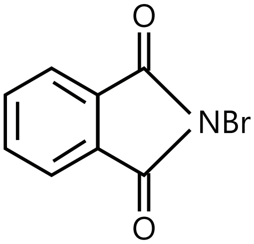
(O)

Q.20 The compound **R** is ***(2016)***

(A) 

(B) 

(C) 

(D) 

Q.21 The compound **T** is ***(2016)***

(A) Glycine (B) Alanine (C) Valine (D) Serine

PlancEssential Questions

JEE Main/Boards

Exercise 1

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

Exercise 2

Q.10 Q.14 Q.19

Previous Years' Questions

Q.1 Q.5 Q.10

JEE Advanced/Boards

Exercise 1

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

Exercise 2

Q.8 Q.19 Q.20
Q.22 Q.28

Previous Years' Questions

Q.2 Q.4

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 A **Q.2** C **Q.3** D **Q.4** B **Q.5** D **Q.6** C
Q.7 D **Q.8** A **Q.9** D **Q.10** B **Q.11** D **Q.12** A
Q.13 D **Q.14** B **Q.15** D **Q.16** B **Q.17** D **Q.18** D
Q.19 B **Q.20** A **Q.21** B **Q.22** A

Previous Years' Questions

Q.1 C **Q.2** A **Q.3** C **Q.4** B **Q.5** C **Q.6** C
Q.7 A **Q.8** A **Q.9** A **Q.10** A **Q.11** A **Q.12** B
Q.13 B **Q.14** C **Q.15** B **Q.16** D **Q.17** A **Q.18** C

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

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

Multiple Correct Choice Type

Q.19 A, B

Comprehension Type

Q.20 B **Q.21** A **Q.22** C **Q.23** B

Assertion Reasoning Type

Q.24 C **Q.25** A **Q.26** D **Q.27** A **Q.28** C **Q.29** B
Q.30 A **Q.31** A

Previous Years Questions

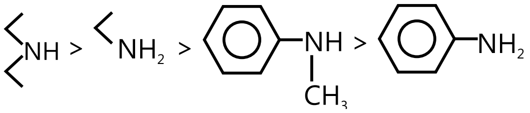
Q.1 B **Q.2** A **Q.3** C **Q.4** A → p; B → q; C → r; D → s **Q.11** B
Q.12 A **Q.13** D **Q.14** A → r, s; B → p, q; C → p, q, r; D → p, s **Q.15** C
Q.16 C **Q.17** A **Q.18** A **Q.19** B **Q.20** A **Q.21** B

Solutions

JEE Mains/Boards

Exercise 1

Sol 1: (i)



(ii) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

(iii) (a) p-nitro aniline < Aniline < p-toluidine

(b) $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$

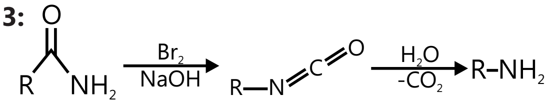
Sol 2: 1° and 2° amines react with acetyl chloride to form acetyl derivatives.

$R{-}NH_2 + CH_3COCl \longrightarrow RNHCOCH_3 + HCl$

$(CH_3)_2{-}NH + CH_3COCl \longrightarrow (CH_3)_2N{-}COCH_3 + HCl$

Tertiary amine do not undergo this reaction.

Sol 3:



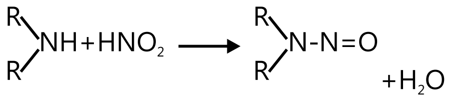
Reaction of a primary amide to form primary amine with one fewer carbon atom.

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

Sol 5: Aliphatic amines

Primary: $RNH_2 + HNO_2 \longrightarrow ROH + H_2O + N_2$

Secondary:



$$R_2NH + HNO_2 \longrightarrow R_2N{-}N{=}O + H_2O$$

Tertiary: $R_3N + HNO_2 \longrightarrow R_3NH^{\oplus} + NO_2^{\ominus}$

Aromatic Amines forms diazonium ions.

Sol 6: (i) Refer Sol.3

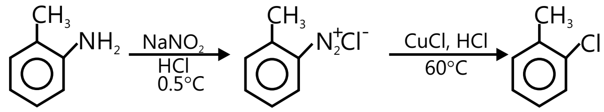
(ii) Refer Gabriel Pthalimide synthesis

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

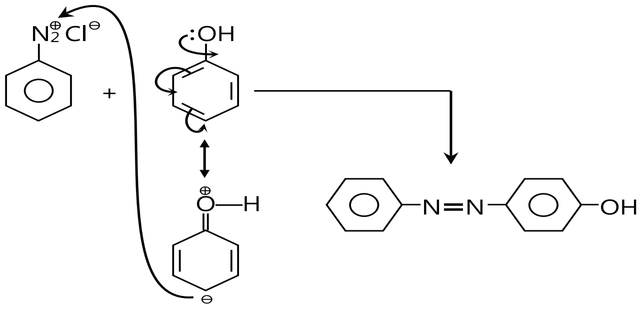
(b) $CH_3NH_2 \longrightarrow CH_3OH \longrightarrow CH_3I \longrightarrow CH_3CN \longrightarrow CH_3CH_2NH_2$

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

Eg.



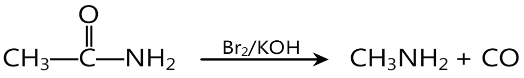
(ii)



Sol 9: (i) Refer to Sol.8 (ii)

(ii) The reaction involves the conversion of an amide into one carbon loss, by action of hypoactive NaOH solution $+Br_2$.

Example:



$$CH_3{-}\overset{O}{\overset{\|}{C}}{-}NH_2 \xrightarrow{Br_2/KOH} CH_3NH_2 + CO$$

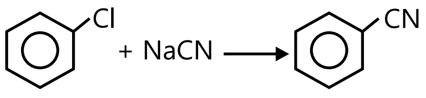
(iii) Acetylation - 1° or 2°C amines react will acetyl chloride acetic anhydride to from acetyl derivatives.

Ex: $CH_3NH_2 + CH_3COCl \longrightarrow CH_3NCOCH_3 + HCl$

Sol 10: (i) 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.

(ii)



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.

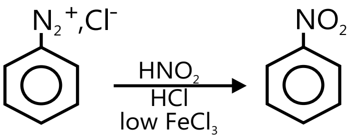
Sol 11: Refer to sol. 2

Sol 12: (i) Aniline is a weaker base as compared to methyl amine as lone pair of NH_2 is delocalised on the ring. Hence pk_B aniline > pk_B methyl amine.

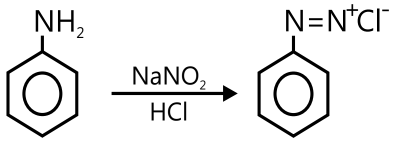
(ii) $MeNH_2$ is a good base in water, it reacts will $FeCl_3$ to form $Fe(OH)_3 + MeNH_4^+Cl^-$

(iii) Due to NH_2 group on aniline, there is extra e^- density on benzene ring. Hence, nucleophilic substitution does not take place.

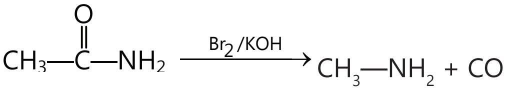
Sol 13: (i)



(ii)



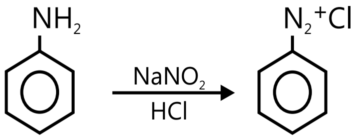
(iii)



$CH_3—\overset{O}{\overset{\|}{C}}—NH_2 \xrightarrow{Br_2/KOH} CH_3—NH_2 + CO$

Sol 14: Factual

Sol 15:



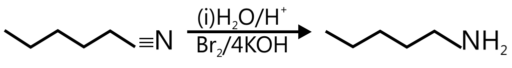
Sol 16: (i) In aromatic amines, the ⊕ charge is delocalised on the less electron -ve ring C- due to good resonance.

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

Sol 17:

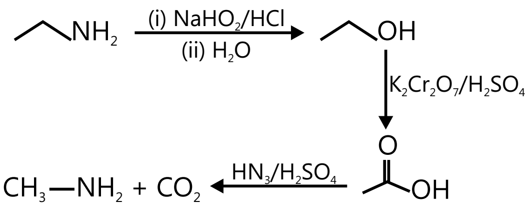
(i) $—COOH \xrightarrow{NH_3/H_2SO_4} CH_3—NH_2$

(ii)

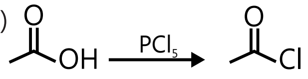


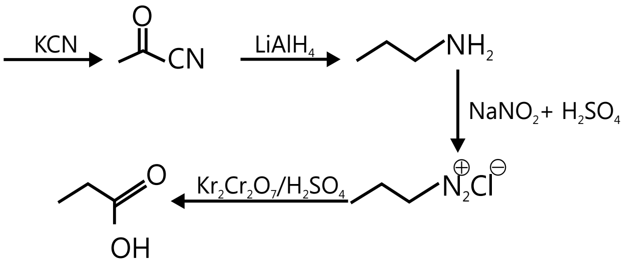
(iii) $CH_3OH \xrightarrow[\text{(ii) 3KOH}]{\text{(i) } CHCl_3/HCl} CH_3—COOH$

(iv)

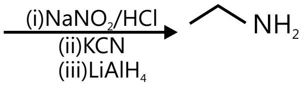


(v)

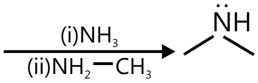




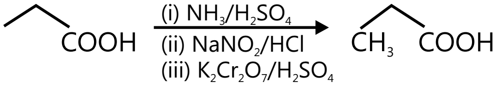
(vi) CH_3NH_2



(vii) CH_3NO_2



(viii)

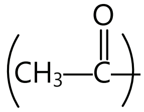


Sol 18: (i) Any reactions which involves two or more equivalent of reactions for proceeding reaction are known as coupling reaction

Exp. Wurtz,Pinacol-pinacolone etc.

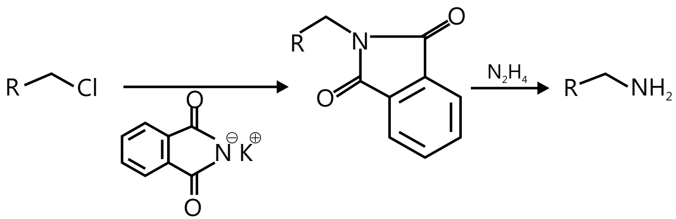
(ii) Addition of ammonia ⟶ Ammonolysis

(iii) Addition of acetyl group

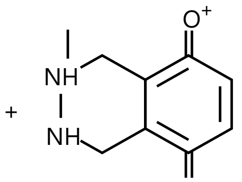


$\left(CH_3—\overset{O}{\overset{\|}{C}}—\right)$ acetylation

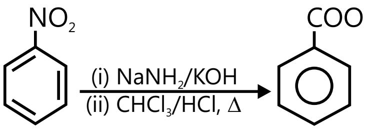
(iv) Gabriel Synthesis:



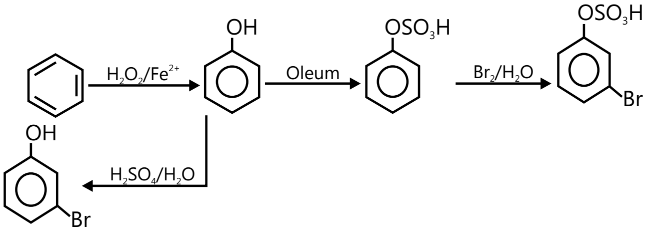
Test for 1° amines



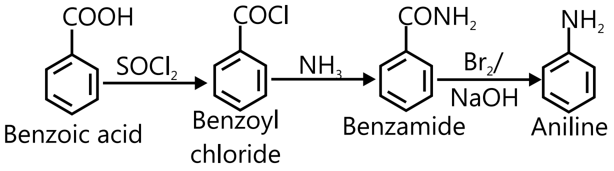
Sol 19: (i)



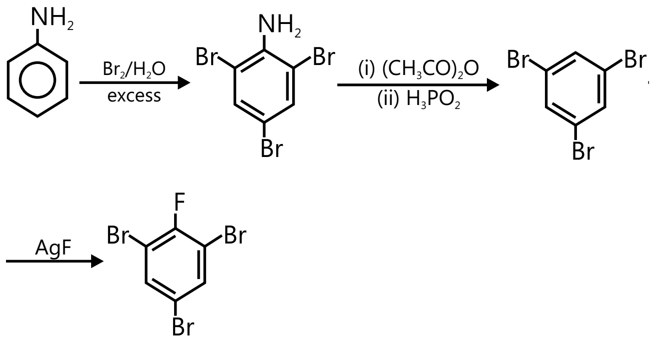
(ii)



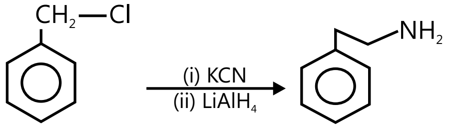
(iii)



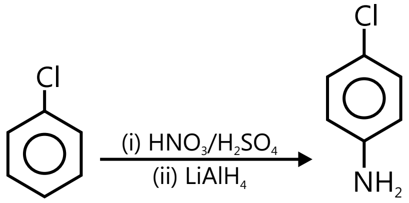
(iv)



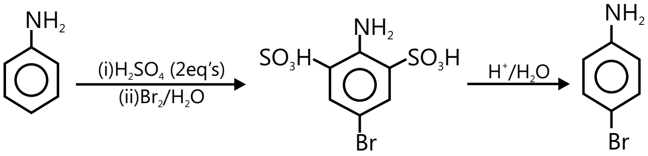
(v)



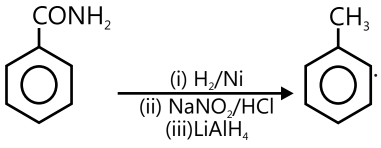
(vi)



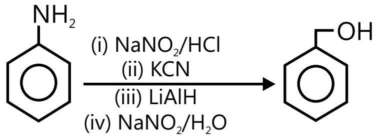
(vii)



(viii)



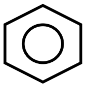
(ix)



Sol 20: Refer Text for Curtius mechanism.

Sol 21: (i) ph—N ≡ C

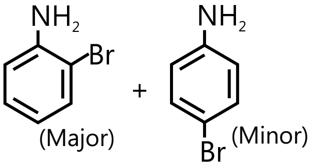
(ii)



(iii) Acid-base reaction ph-$\overset{\oplus}{N}H_3 + H_2SO_4^-$

(iv) phOEt

(v)



(vi) Acetophenone

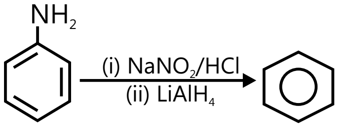
(vii) Nitrobenzene

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

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

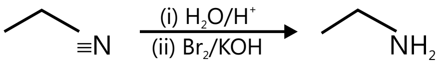
(iii) In aromatic amines,they have lone pair of N in conjugation with ring ⇒ less basic

Sol 23: (i)



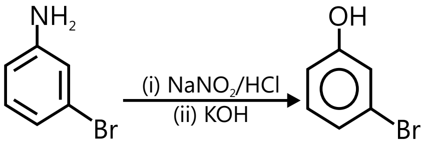
(ii) $CH_3NH_2 \xrightarrow[\text{(ii) KCN}]{\text{(i) NaNO}_2\text{/HCl}} CH_3CN$

(iii)

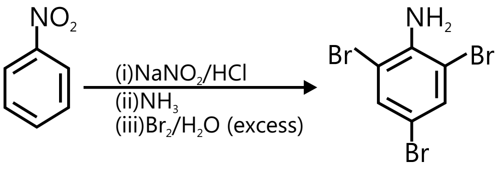


Schmidt reaction

(iv)

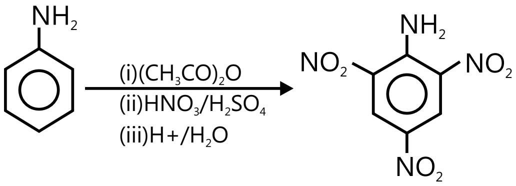


(v)



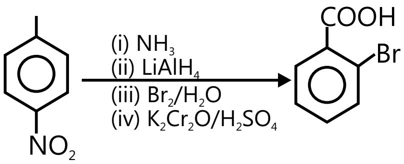
Sol 24: Intramolecular acid-base reactions of molecule (like some amine + carboxylic acid in same molecule)

Sol 25:

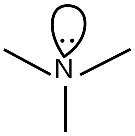


Sol 26: because carbocation intermediate in Friedel craft alkylation reach with l.p. of N in aniline

Sol 27:



Sol 28:

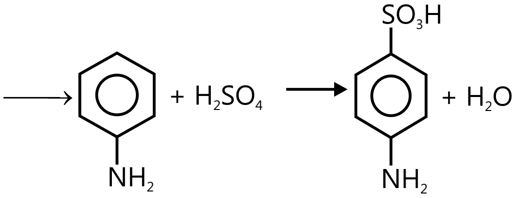


due to flipping it is considered as planar molecule.

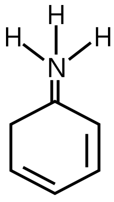
Exercise 2

Single Correct Choice Type

Sol1:(A) (i)



Sol 2: (C)



Not acceptable

Nitrogen can't form 5 bonds

Sol 3: (D) Order of basic strength

4 > 3 > 2 > 1 Basic strength ∝ +I effect

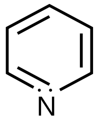
Sol 4: (B) 1 > 2 > 3

Sol 5: (D) Primary amines gives carbylamine test.

Sol 6: (C) End product has a hydrophobic and a hydrophilic part.

Sol 7: (D) s > t > p > NH_3

Sol 8: (A)



localised lone pair

Sol 9: (D) $CH_3NO_2 \xrightarrow[NaOH]{Cl_2} CH_2ClNO_2 \xrightarrow[NaOH]{Cl_2}$

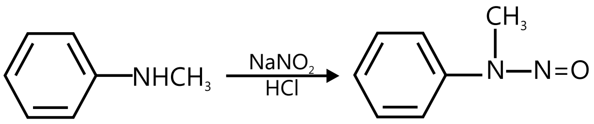
$CHCl_2NO_2 \xrightarrow[NaOH]{Cl_2} CCl_3NO_2$

CH_3NH_2 is not formed

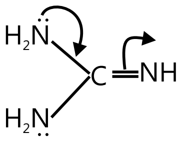
Sol 10: (B) Br_2/NaOH

$R—CH_2CONH_2 \xrightarrow[NaOH]{Br_2} R—CH_2–CH$

Sol 11: (D)



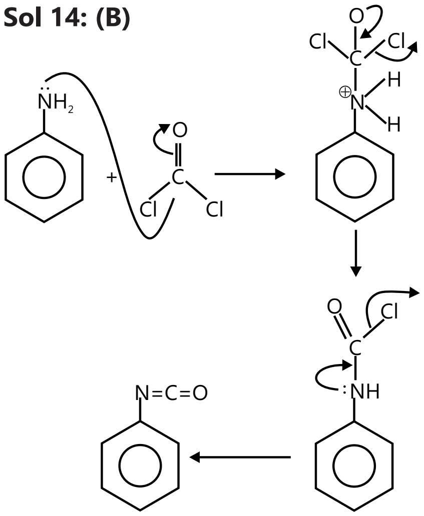
Sol 12: (A)



Sol 13: (D) All of these

$K_2Cr_2O_7$ is a strong oxidising agent.

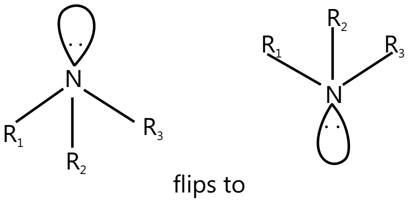
Sol 14: (B)



Sol 15: (D) $CH_3—CH_2—NH_2 + KMnO_4 \longrightarrow CH_3CHO$

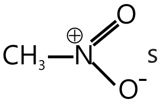
Sol 16: (B) Baker-Mulliken's Test is a test for nitrocompounds.

Sol 17: (D)



Due to flipping, tertiary amine is a racemic mixture.

Sol 18: (D)



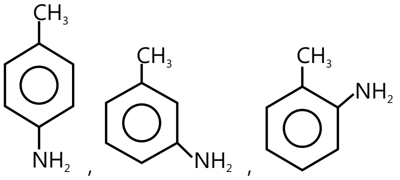
$CH_3—\overset{\oplus}{N}(=O)O^-$ shows H-bonding,

α -halogenation as well as tautomerism.

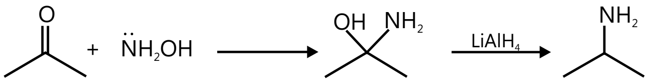
Sol 19: (B) Nitrobenzene on reduction with Sn/HCl gives aniline. With Zn it gives phenyl hydroxylamine. With methanolic NaOMe nitrobenzene gives Azoxybenzene. On reaction with Zn and strong base it gives Hydrazobenzene.

Sol 20: (A) $\underset{\text{tertiary}}{RCN} < \underset{\text{secondary}}{RCH=NR} < \underset{\text{primary}}{RH_2N}$

Sol 21: (B)



Sol 22: (A)



Previous Years' Questions

Sol 1: (C) Self- explanatory

Sol 2: (A) $\underset{\text{(Acetamide)}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow[-2H_2O]{}$

$\underset{\text{(Methyl amine)}}{CH_3NH_2} + 2KBr + 2K_2CO_3$

Sol 3: (C) Hofmann degradation of amide

$R–CONH_2 + Br_2 + 4KOH \longrightarrow$

$\underset{\text{(primary amine)}}{R-NH_2} + 2KBr + K_2CO_3 + 2H_2O$

Sol 4: (B) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$

$K_b = 5.4 \times 10^{-4}, 4.5 \times 10^{-4}, 0.6 \times 10^{-4}$

Sol 5: (C) $(CH_3)_2NCOCH_3 + HCl/H_2O \longrightarrow$

$(CH_3)_2NH + CH_3COOH$

Sol 6: (C) Secondary>tertiary>primary

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.

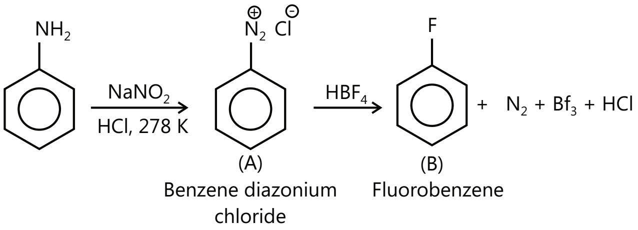
$R\overset{+}{N} \equiv \overset{-}{C} + H_2O \rightarrow RN = CHOH \rightarrow \underset{\text{Alkyl Formamide}}{RNHCHO}$

Sol 11: (A) self-explanatory

Sol 12: **(B)** Due to strong deactivation of benzene ring by $–NO_2$ group, nitrobenzene is often used as a solvent in Friedel–Craft's reaction.

Sol 13: (B) $-NO_2$ is electron withdrawing which will destabilize σ - complex.

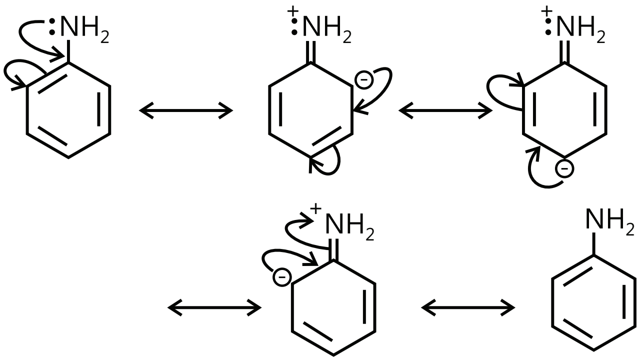
Sol 14: (C)



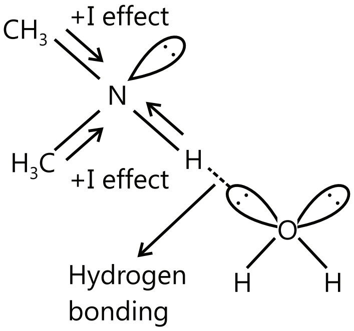
Sol 15: (B) Molisch's Test: when a drop or two of alcoholic solution of a–naphthol is added to sugar solution and then conc. H_2SO_4 is added along the sides of test tube, formation of violet ring takes place at the junction of two liquids.

Sol 16: (D) $R-CH_2-NH_2 \xrightarrow[C_2H_5OH]{CHCl_3/KOH} R-CH_2-NC$

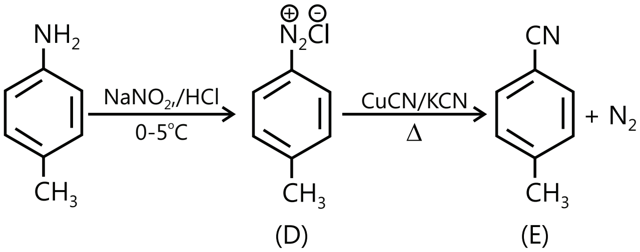
Sol 17: (A) Among $C_6H_5NH_2$, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$. $C_6H_5NH_2$ is least basic due to resonance.



Out of $(CH_3)_3N$, CH_3NH_2, $(CH_3)_2NH$. $(CH_3)_2NH$ is most basic due to +I effect and hydrogen bonding with H_2O.



Sol 18: (C)

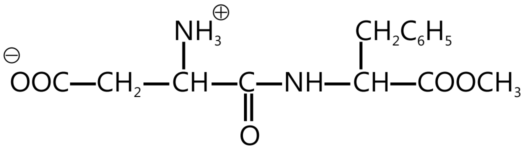


JEE Advanced /Boards

Exercise 1

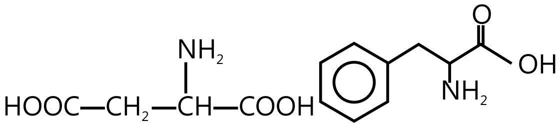
Sol 1: (i) Carboxylic acid, amine, ester

(ii)



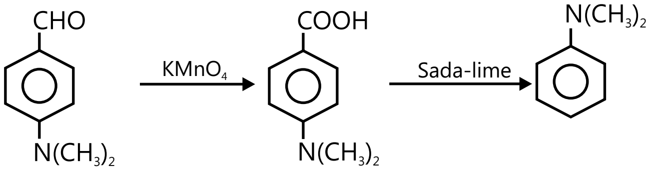
$$^{\ominus}OOC-CH_2-\underset{}{\overset{\overset{\oplus}{NH_3}|}{CH}}-\underset{\underset{O}{\|}}{C}-NH-\overset{CH_2C_6H_5|}{CH}-COOCH_3$$

(iii) Aspartic acid and phenylalanine

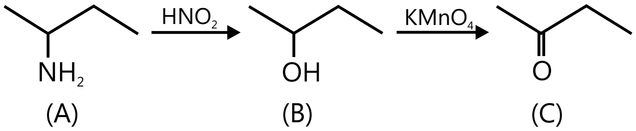


(iv) Phenylalanine is more hydrophobic because of the benzyl side chain.

Sol 2:

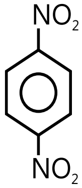


Sol 3:

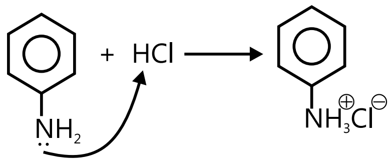


Other isomers are primary amines.

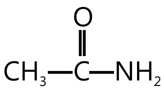
Sol 4:



Sol 5: (i)



(ii) $CH_3-CH_2-\ddot{N}H_2$ Ethylamine

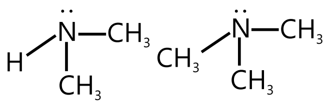


$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ Acetamide

Ethylamine is basic due of the presence of localised lone pair.

Acetamide is acidic due to the presence of acidic hydrogen.

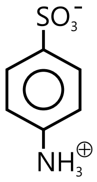
(iii)



Dimethylamine Trimethylamine

More steric hinderance in Trimethylamine

(iv) It forms zwitter ion



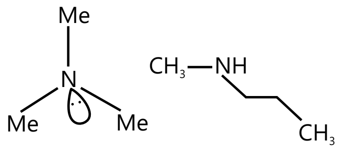
Sol 6: (i) Amine group in glycine is more basic.

(ii) More equivalent resonance structures

(iii) It stabilises the complex.

(iv) Because of side products

Sol 7: (i)



n-propylamine forms H-bond.

(ii) Steric hinderance in trimethylamine

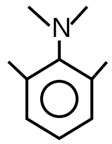
(iii) Due of formation of a soluble complex salt

$AgCl + 2CH_3NH_2 \longrightarrow [Ag(CH_3NH_2)_2]^+Cl^-$

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

(ii) No N—H bond in tertiary amine.

(iii)



Steric hinderance of 2 Me groups present on benzene ring.

(iv) In (I) lone pair is localized, Inductive effect of 'O' in (III)

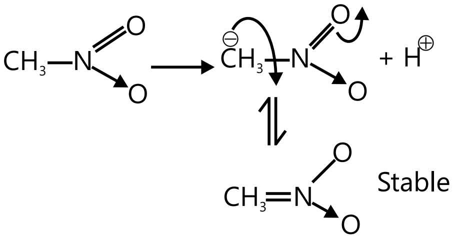
In IV the lone pair is delocalised

I > II > III > IV

Sol 9: (i) Steric hinderance

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

(iii)



(iv) 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.

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

Sol 10:

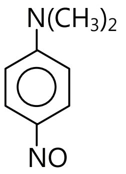
(i) $C=C_6H_5COCl$ $D=C_6H_5CONH_2$

$E=C_6H_5CHNH_2$

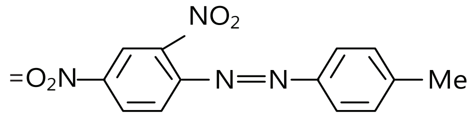
(ii) $F=C_6H_5CN$; $G=C_6H_5COOH$

(iii) H=EtNHBr

(iv) I=



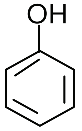
(v) J =



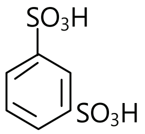
(vi) $K=C_6H_5SO_3H$; $L= C_6H_5SO_3Na$

$M= C_6H_5OH$

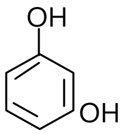
(vii) I = NaOH N =



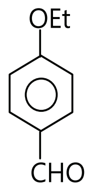
(viii) O =



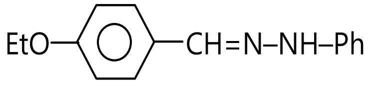
P =

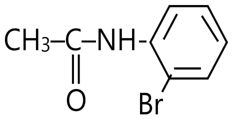


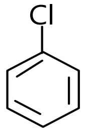
(ix) Q = Ph–O–Et R =

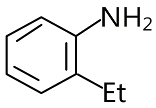
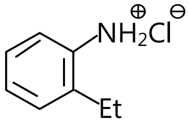


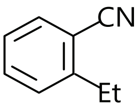
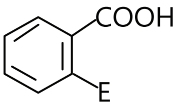
S =

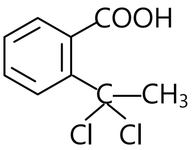
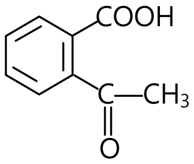


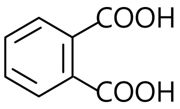
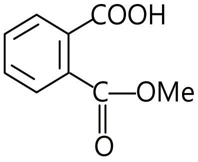
(x) T =  + para isomer

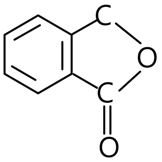
(xi) U = Cu Powder V =  + N_2

Sol 11: (A)  (B) 

(C)  (D) 

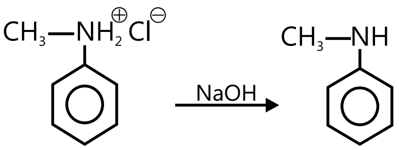
(E)  (F) 

(G)  (H) 

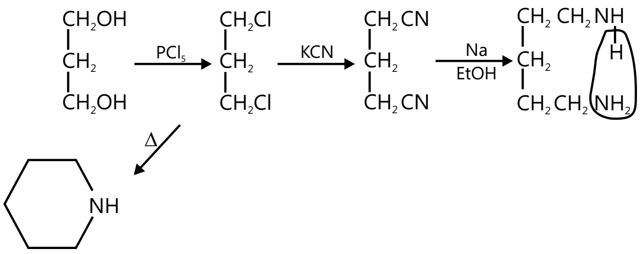
(I) 

Sol 12: $C_2H_5NH_2CH_3—CH_2—NH_2$

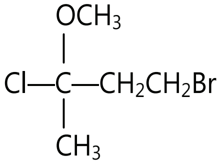
Sol 13:

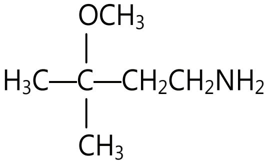


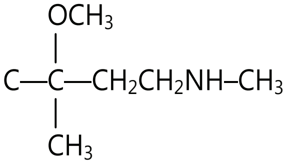
Sol 14:

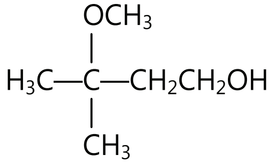


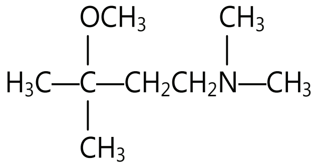
Sol 15:

(A) 
$Cl—\overset{OCH_3}{\underset{CH_3}{C}}—CH_2CH_2Br$

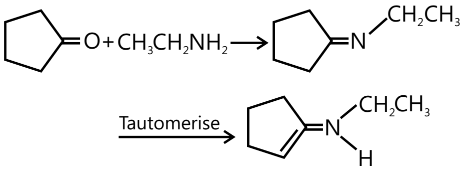
(B) 
$H_3C—\overset{OCH_3}{\underset{CH_3}{C}}—CH_2CH_2NH_2$

(C) 
$C—\overset{OCH_3}{\underset{CH_3}{C}}—CH_2CH_2NH–CH_3$

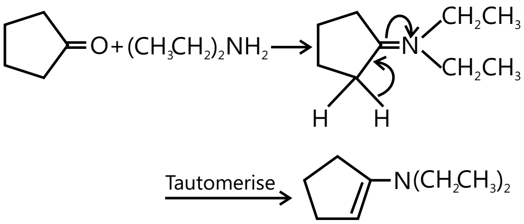
(D) 
$H_3C—\overset{OCH_3}{\underset{CH_3}{C}}—CH_2CH_2OH$

(E) 
$H_3C—\overset{OCH_3}{\underset{CH_3}{C}}—CH_2CH_2\overset{CH_3}{N}—CH_3$

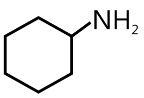
Sol 16 (i)

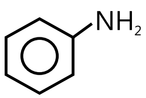


(ii)



Sol 17:


Cyclohexylamine


Aniline

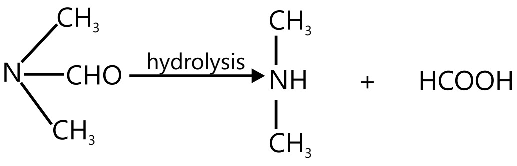
Lone pair of nitrogen in aniline is delocalized due to resonance.

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.

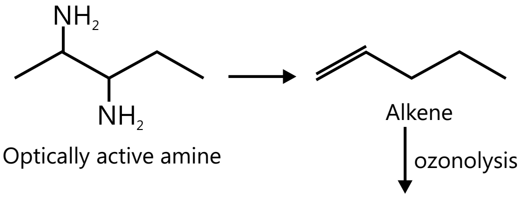
Sol 20: Although inductive effect of alkyl groups is greater in trimethylamine but the alkyl groups crowds the nitrogen atom and reduces its basicity.

Sol 21:



(A) (B) (C)

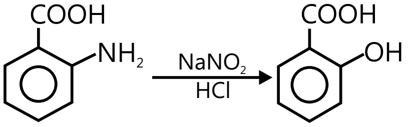
Sol 22:



$HCHO + CH_3CH_2CH_2CHO$

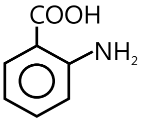
No, there is no structural isomer possible.

Sol 23:

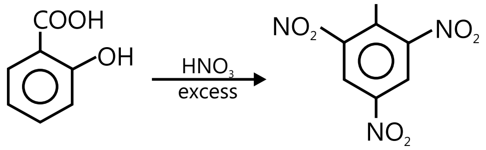


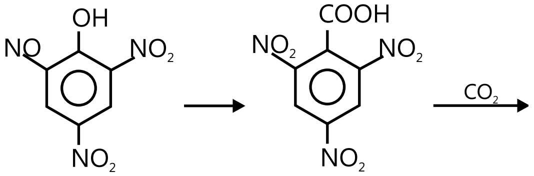
The compound gives +ve less for NH_2 and COOH

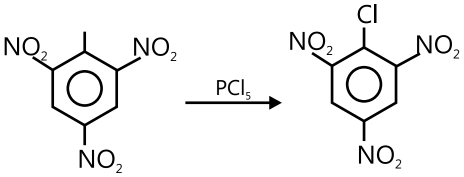
∴ A is



B =







Sol 24: $C_8H_8O \xrightarrow{NH_2OH.HCl} B + C$
Ketone/

$B \xrightarrow{acid} D$

$C \xrightarrow{acid} E$

D + alc. KOH $\longrightarrow$ F

F + $CH_3COCl \longrightarrow$ D

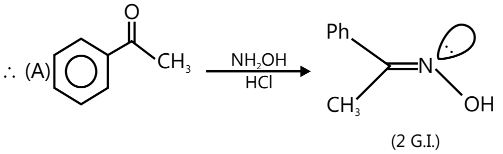
E alkali $\longrightarrow$ acid/solid $C_7H_6O_3$ (G)

$C_8H_8O \longrightarrow$ Double bond equivalent

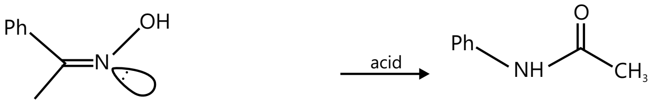
DBE = $\frac{1}{2}((16+2)–8) = 5 \longrightarrow$ benzene ring and a π bond outside.

∴ $NH_2OH/HCl \longrightarrow$ 2 product (G.I.)

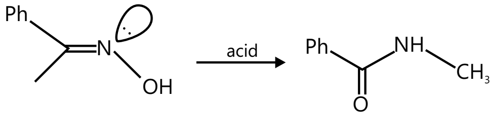
∴ It is a ketone.



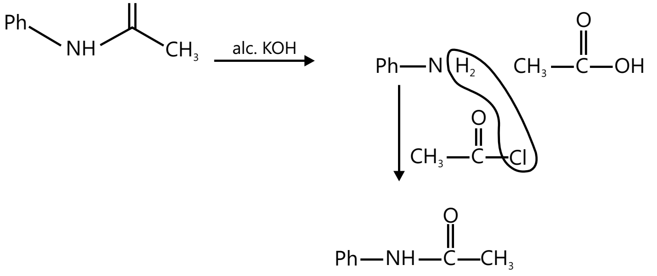
(2 G.I.)
cis and trans

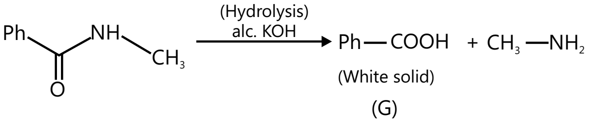


(B) (Beckman Rearrangement) (D)



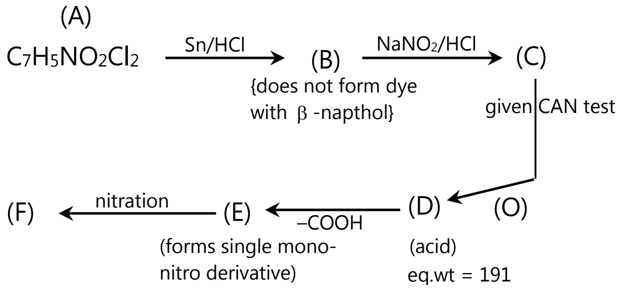
(E)

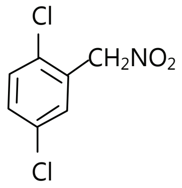


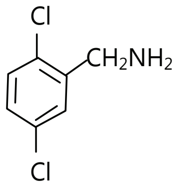


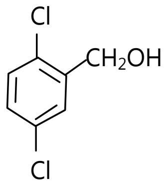
(E) (G)

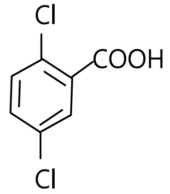
Sol 25:



(A)


(B)


(C)


(D)


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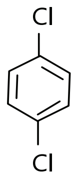
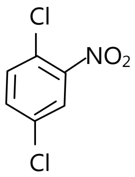


(F)


Sol 26: $\therefore NH_4^+$

as gas is NH_3

M.W. 135 $\xrightarrow{-NH_2\ +\ OH}$ B mole IRH

A + NaOH $\xrightarrow{alc.}$ R—CH_2COOH $\longrightarrow$ Mass of R =

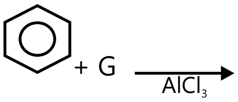
R—CH_2—NH_2 $\xrightarrow{HNO_2}$ RCOOH (B)

A $\xrightarrow{Br_2/KOH}$ C primary amine R–CH_2–NH_2

R–CH_2–$CONH_2$ (C) $\xrightarrow[HNO_2]{cold}$ (D) Primary amine $\xrightarrow[cold\ CAN]{red}$

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

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

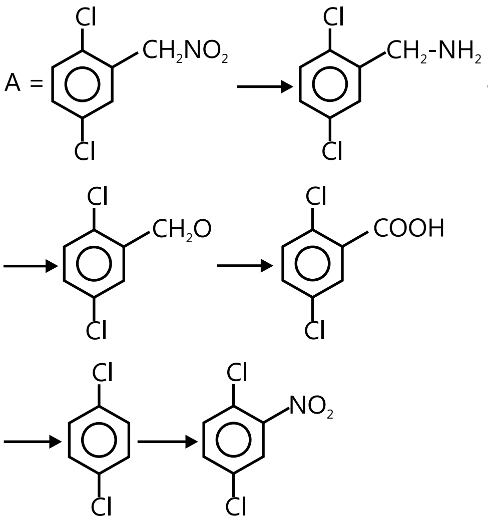


B = $C_7H_5NH_2Cl_2$ does not give compound B-does not form a dye with β-naphthol

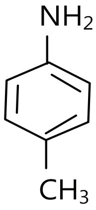
∴ A is (C) is a primary alcohol.

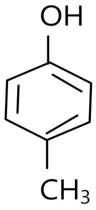
as de-carboxylation gives single derivatives

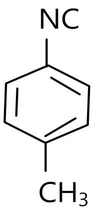
∴ Cl should be symmetrically oppositely placed.

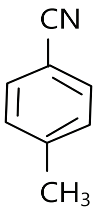


Sol 27:

(A)


(B)


(C)


(D)


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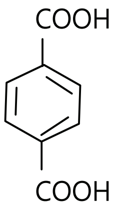


Sol 28: Degree of unsaturation of A = 2 since A forms hydrochoride, it contain both a basic and acidic functional group. It's most likely to be an amino acid. On decarboxylation, it forms an amine B, Degree of unsaturated of B = 0

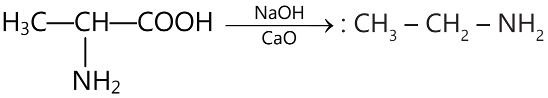
∴ B is saturated amine.

∴ B $\xrightarrow[HCl]{NaNO_2}$ give C_2H_5OH (E)

∴ B is $CH_3CH_2NH_2$

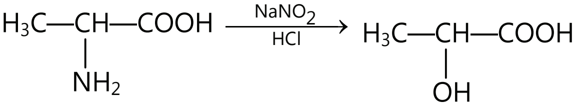
$\xrightarrow[HCl]{NaNO_2}$ C (a hydroxyl acid) Which yeilds cyclic diester on heating

∴ Reactions



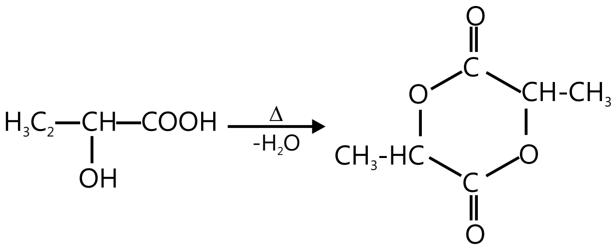
$$H_3C-\underset{NH_2}{\underset{|}{CH}}-COOH \xrightarrow[CaO]{NaOH} : CH_3-CH_2-NH_2$$

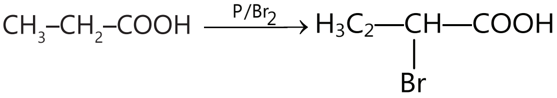
$$CH_3-CH_2-NH_2 \xrightarrow[HCl]{NaNO_2} CH_3CH_2OH$$



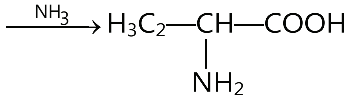
$$H_3C-\underset{NH_2}{\underset{|}{CH}}-COOH \xrightarrow[HCl]{NaNO_2} H_3C-\underset{OH}{\underset{|}{CH}}-COOH$$

(c)





$$CH_3\text{–}CH_2\text{–}COOH \xrightarrow{P/Br_2} H_3C_2-\underset{Br}{\underset{|}{CH}}-COOH$$



$$\xrightarrow{NH_3} H_3C_2-\underset{NH_2}{\underset{|}{CH}}-COOH$$

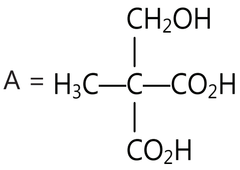
Sol 29: (A) $C_5H_8O_5 \longrightarrow$ (B) $C_4H_8O_3 \xrightarrow{H_2SO_4}$

$C \xrightarrow[\text{alkyl ester}]{} \xrightarrow{H_2} D \xrightarrow{\text{conc. } NH_3} E\ (C_4H_9OH)$

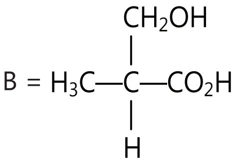
$C_3H_9N \xleftarrow[KOH]{Br_2} (C_4H_9OH)$

degree of unsaturation = 2 × 5 + 2 – 8

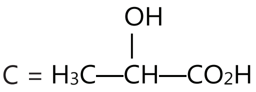
= 4 – 2 = 2



$$A = H_3C-\overset{CH_2OH}{\overset{|}{\underset{CO_2H}{\underset{|}{C}}}}-CO_2H$$



$$B = H_3C-\overset{CH_2OH}{\overset{|}{\underset{H}{\underset{|}{C}}}}-CO_2H$$



$$C = H_3C-\overset{OH}{\overset{|}{CH}}-CO_2H$$

D = $(CH_3)_2CHCO_2C_2H_5$

E = $(CH_3)_2$ $CHCONH_2$

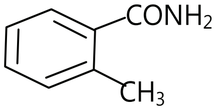
F = $(CH_3)_2$ $CHNH_2$

G = $(CH_3)_2$ CHOH

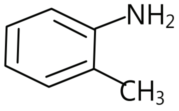
H = CH_3COCH_3

Sol 30:

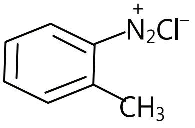
(A)



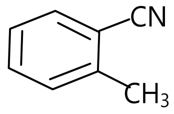
(B)



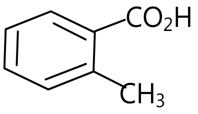
(C)



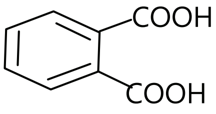
(D)



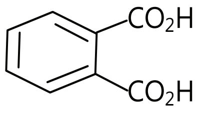
(E)



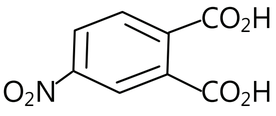
(F)



(G)



(H)



Exercise 2

Single Correct Choice Type

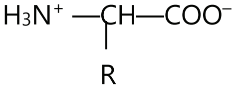
Sol 1: (B) Propyne- Forms a precipitate with $AgNO_3$ in ethanol.

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

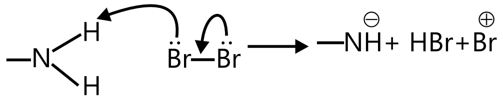
Acetaldehyde- Reduces Fehling's solution

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

Sol 2: (D) Acetic acid

Sol 3: (C) 
$$H_3N^+-\underset{\displaystyle R}{\underset{|}{C}H}-COO^-$$

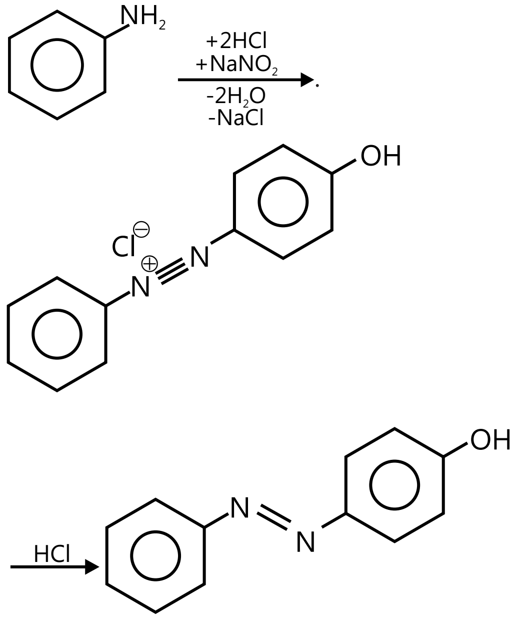
Sol 4: (C)

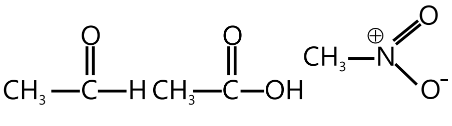


Sol 5: (B) Ethylnitrile (CH_3CN)

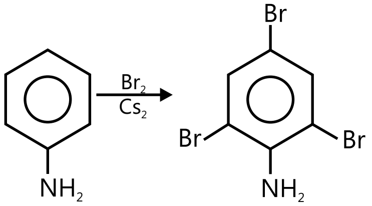
Sol 6: (C) The lone pair of electron on nitrogen atom in aniline is delocalized over aniline.

Sol 7: (B) $R-\ddot{N}H_2$ behave as a base in weakly acidic medium



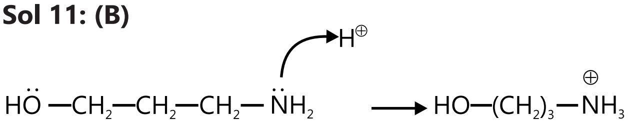
Sol 8: (B) 
$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H \quad CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH \quad CH_3-\overset{\oplus}{N}\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O^-}$$

All three shows acidic behaviour.

Sol 9: (C) 

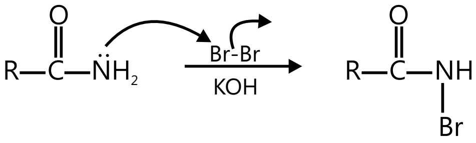
Sol 10: (C) Gabriel-phthalimide synthesis.

Sol 11: (B)



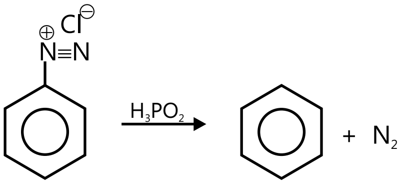
Sol 12: (A) 2 > 1 > 3

Consider inductive effect of primary, secondary and tertiary law.

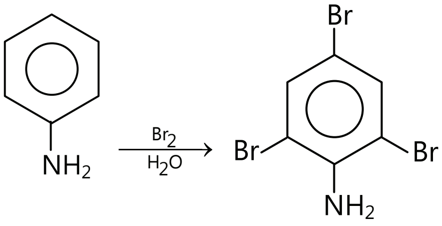
Sol 13: (A) 

Sol 14: (D) Self-explanatory

Sol 15: (C)



Sol 16: (C)



Sol 17: (C) Secondary amine

Sol 18: (B) Trihalogenated amine and a primary amine

Multiple Correct Choice Type

Sol 19: (A, B) 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.

Comprehension Type

Sol 20: (B) $NO_2 \longrightarrow$ –M effect

$CH_3 \longrightarrow$ +Z effect

$OCH_3 \longrightarrow$ mid +M effect

$NMe_2 \longrightarrow$ high +M effect

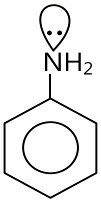
Sol 21: (A) –I effect of –OMe

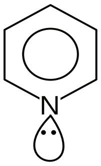
Sol 22: (C) +M effect of –OMe at para position

Sol 23: (B) The product formed when bromobenzene reacts with benzenediazonium chloride in presence of NaOH is p-Bromodiphenyl

Assertion Reasoning Type

Sol 24: (C)

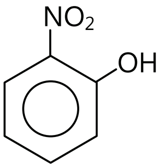


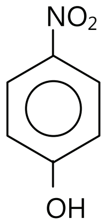


Sol 25: (A) False lone pair is delocalised of Ph-NH_2 whereas its localised for aniline .

Self Explanatory

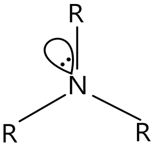
Sol 26: (D)





NO_2 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 27: (A)

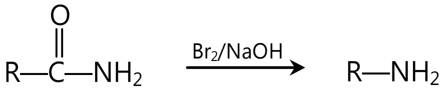


Large size less solvate or hence less basic.

Sol 28: (C) 3° amine cannot be synthesised using Gabriel phthalimide

Sol 29: (B) Both statements are true but 4-nitrochlorobenzene goes nucleoliphilic 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 30: (A)

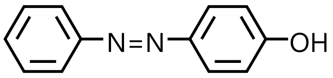


$R-\overset{\overset{O}{\|}}{C}-NH_2 \xrightarrow{Br_2/NaOH} R-NH_2$

Sol 31: (A) Self explanatory (refer to theory of reaction)

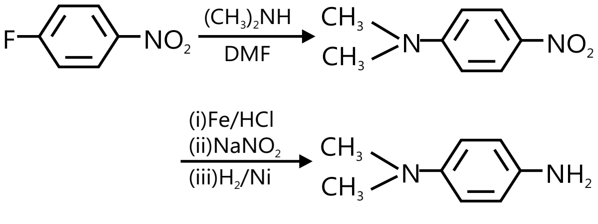
Previous Years' Questions

Sol 1: (B) $C_6H_5N_2^+Cl^- + C_6H_5OH \longrightarrow$

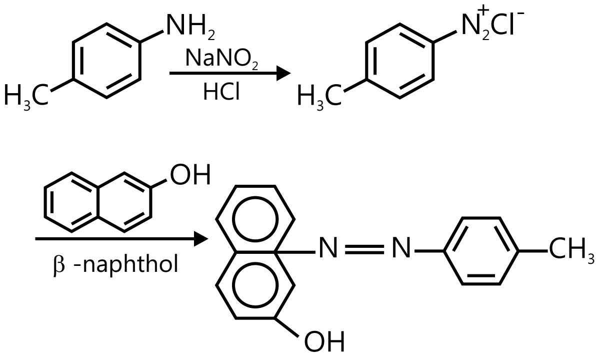


p-hydroxy azobenzene

Sol 2: (A)



Sol 3: (C) As we know, benzenediazonium salt forms brilliant coloured dye wit h 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.

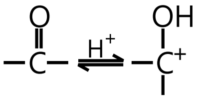


Sol 4: A → p; B → q; C → r; D → s

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.

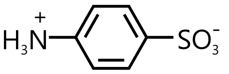


$$-\overset{\overset{O}{\|}}{C}- \overset{H^+}{\rightleftharpoons} -\overset{\overset{OH}{|}}{\underset{|}{C^+}}$$

As H^+ concentration rises sufficiently, a large number of molecules of hydrazine gets converted into hydrazonium 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.

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

Sol 6: Zwitter ionic:

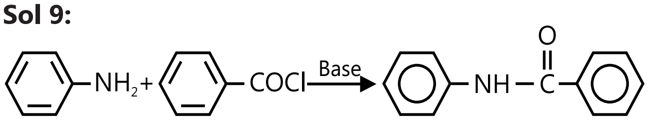


sulphanilic acid

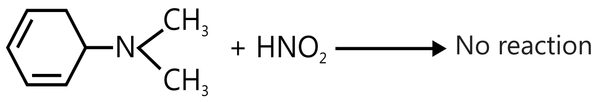
Sol 7: $C_6H_5NH_2 + NaNO_2 \xrightarrow[0°C]{HCl} C_6H_5N_2^+Cl^- \xrightarrow[heat]{CuCl} C_6H_5–Cl$

Sol 8: C_6H_6 + conc.HNO_3/conc.H_2SO_4 $\rightarrow C_6H_5–NO_2 \xrightarrow{Zn–HCl} C_6H_5–NH_2$ (aniline)

Sol 9:

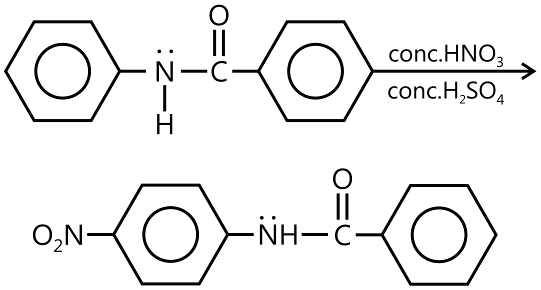


Sol 10:



Tertiary amine does not react with nitrous acid.

Sol 11: (B)

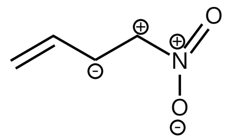


Due to presence of lone pair of electron on nitrogen atom, it will activate the ring and it will stabilize intermediate cation at o and p positions.

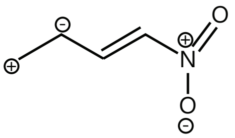
Hence (B) is correct

Sol 12: (A) Same charges are present at nearest position (Less stable)

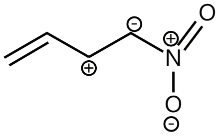
(A)



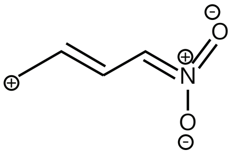
(C)



(B)



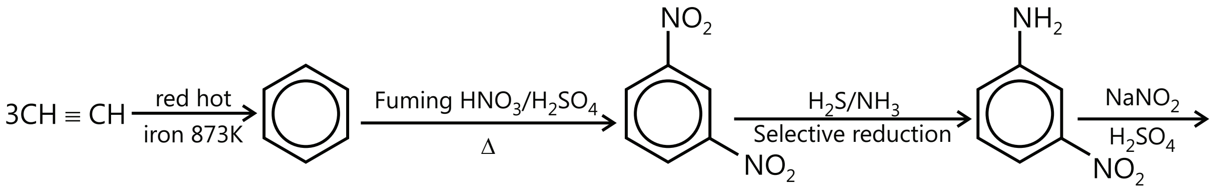
(D)

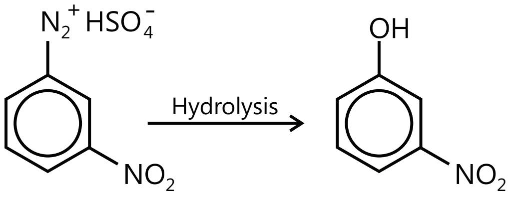


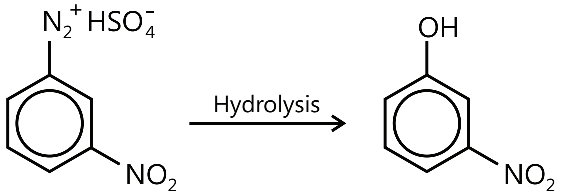
Sol 13: (D) $C_6H_5N_2^{\oplus}Cl^{\ominus}$ gives scarlet red coloured dye with β-naphthol

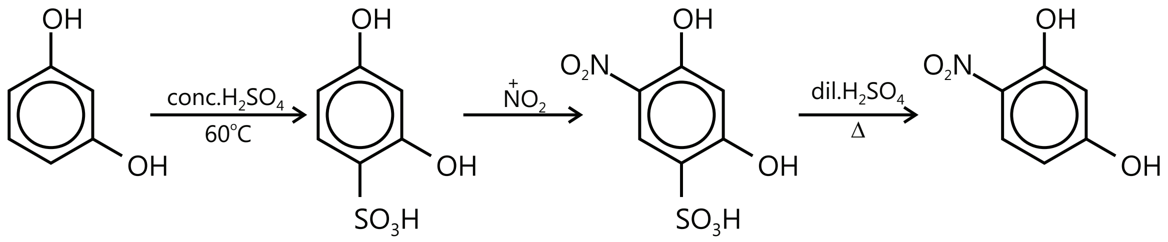
Sol 14: A → r; s B → p, q; C → p, q, r; D → p, s

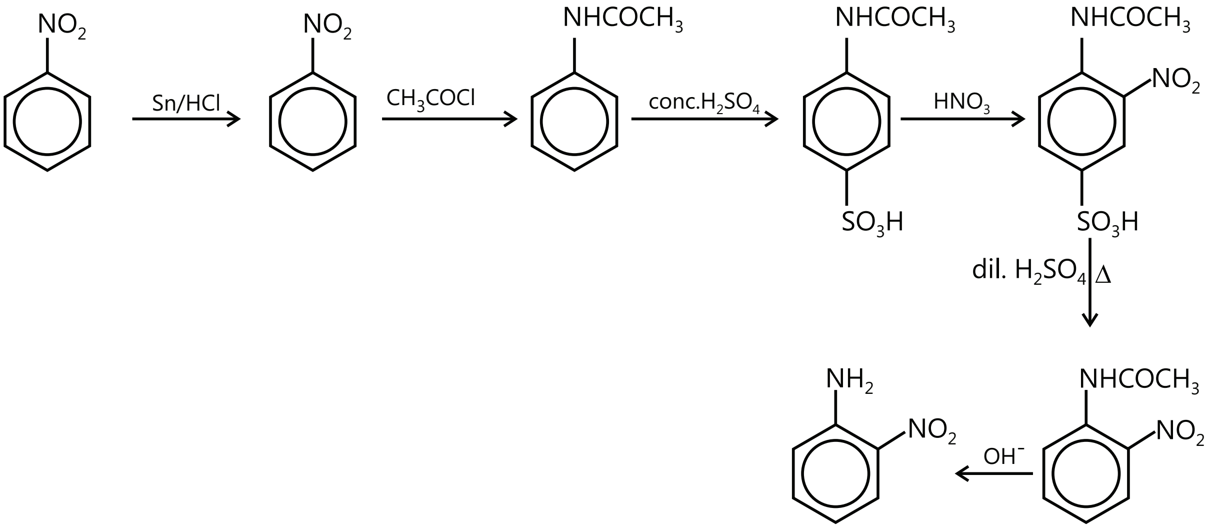
Sol 15: (C)

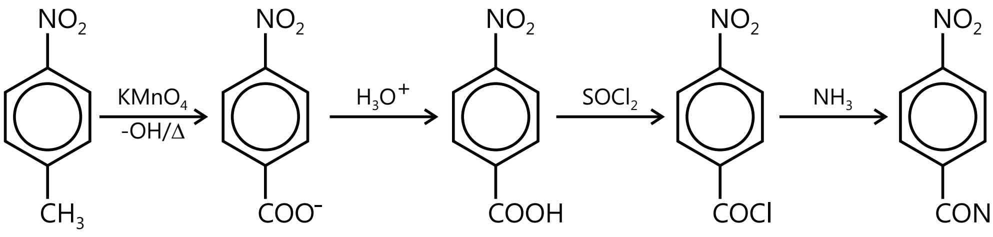

3CH ≡ CH
red hot
iron 873K
Fuming HNO3/H2SO4
Δ
NO2
NO2
H2S/NH3
Selective reduction
NH2
NO2
NaNO2
H2SO4


N2+ HSO4-
NO2
Hydrolysis
OH
NO2

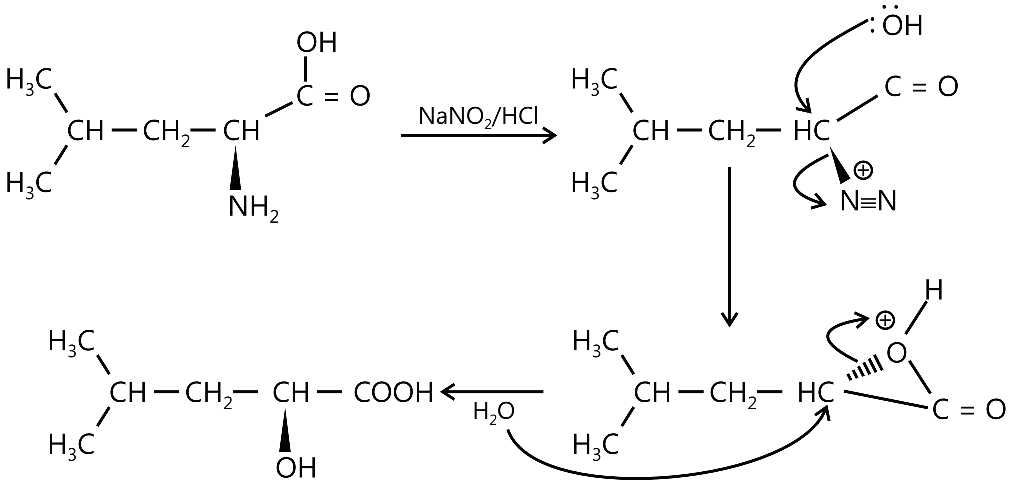

N2+ HSO4-
NO2
Hydrolysis
OH
NO2


OH
OH
conc.H2SO4
60°C
OH
OH
SO3H
NO2+
O2N
OH
OH
SO3H
dil.H2SO4
Δ
O2N
OH
OH

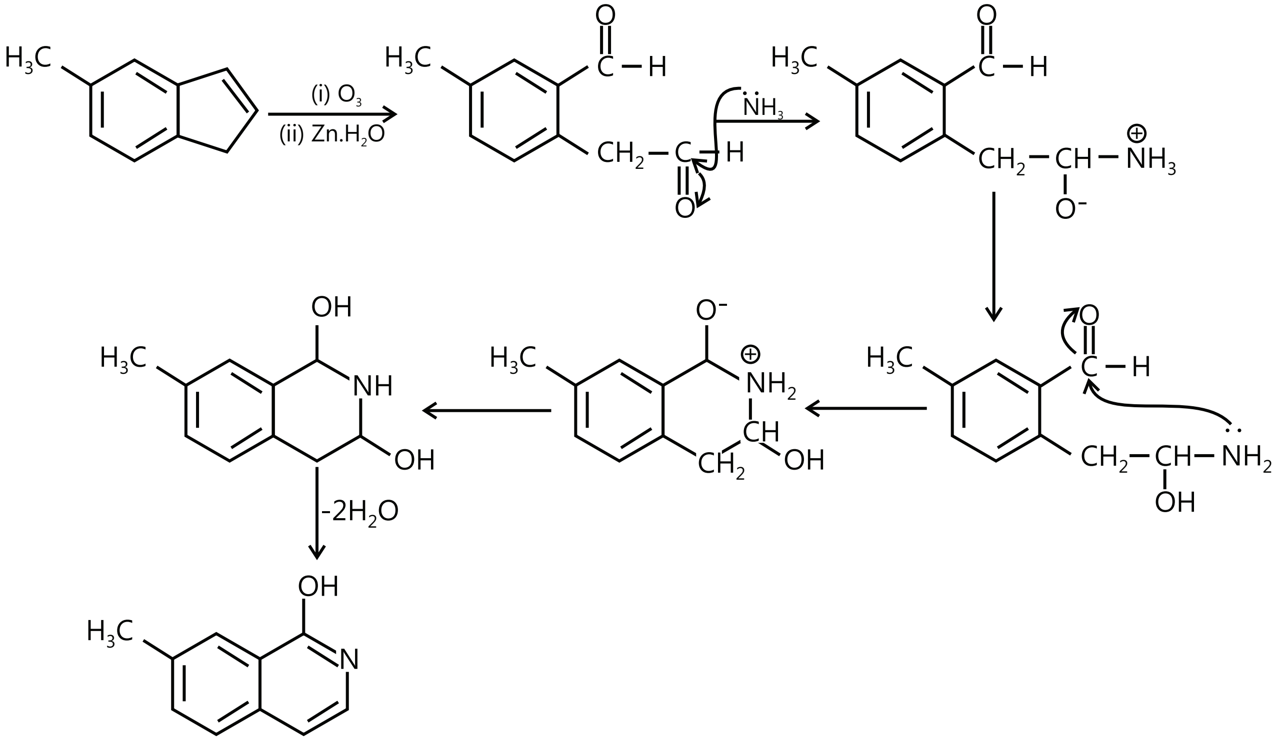

NO2
Sn/HCl
NO2
CH3COCl
NHCOCH3
conc.H2SO4
NHCOCH3
SO3H
HNO3
NHCOCH3
NO2
SO3H
dil. H2SO4 Δ
NHCOCH3
NO2
OH-
NH2
NO2


NO2
CH3
KMnO4
-OH/Δ
NO2
COO-
H3O+
NO2
COOH
SOCl2
NO2
COCl
NH3
NO2
CONH2

Sol 16: (C)

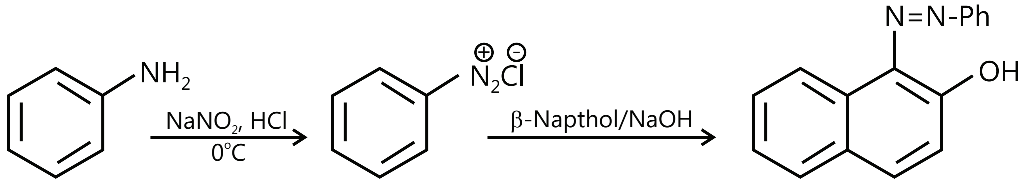


Sol 17: (A)



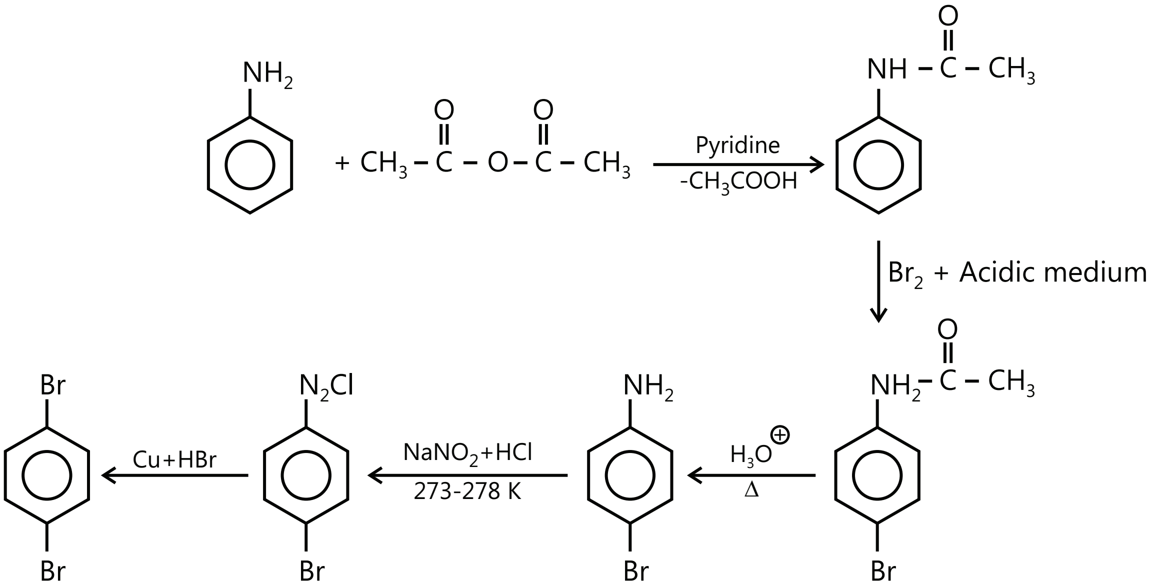
(S)

Sol 18: (A)



(V) (W)

Sol 19: (B)



Sol 20 and 21 (A) and (B):