Solution

CET25C9 AMINES

Class 12 - Chemistry

1.

(**d**) C₆H₅NHCH₃

Explanation: C₆H₅NHCH₃

2.

(c) NO^+_2

Explanation: NO⁺₂ Nitronium ion electrophile initiates the process of nitration of benzene. It is obtained as:

 $\begin{array}{l} H_2SO_4(conc.) \longrightarrow H^+ + HSO_4^- \\ H^+ + HNO_3 \longrightarrow H_2NO_3^+ \\ H_2NO_3^+ \longrightarrow NO_2^+ + H_2O \end{array}$

3.

(d) Benzene sulphonyl chloride

Explanation: Benzene sulphonyl chloride, $C_6H_5SO_2Cl_2$, is called Hinsberg reagent. It is used to distinguish between primary, secondary and tertiary amines.

4. (a) Nucleophilic substitution reaction (SN₂)

Explanation:

- The reaction of phthalimide with KOH removes the **N-H** proton giving an imide ion, which is a good nucleophile.
- Nucleophilic substitution (SN₂) by the imide ion on the alkyl halide generates an intermediate, N-alkyl phthalimide

phthalimide

• Hydrolysis or hydrazinolysis liberates a primary alkyl amine. Therefore, it is a nucleophilic substitution reaction.

5.

(c) III > II > I

Explanation: III > II > I

6.



7.

(b) Br₂+ NaOH

Explanation: Conversion of amide to amine having one carbon less is known as Hoffmann bromide reaction. $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

8.

(b) Primary amines

Explanation: In Gabriel Phthalimide reaction, the sodium or potassium salt of phthalimide is N-alkylated with a primary alkyl halide to give the corresponding *N*-alkylphthalimide for producing primary amines. This is because of the reaction of sodium or potassium salt of phthalimide with alkyl halide impure SN₂ reaction.

9.

(d) Coupling reaction

Explanation: In Coupling reaction, benzene and phenol get coupled through -N=N- linkage. The compounds containing this type of linkage are called azo compounds.

 $C_6H_5N_2^+Cl^- + C_6H_5OH \rightarrow p-C_6H_5N=NC_6H_4OH (dye)$

10.



Explanation: Aniline is a weaker base than NH_3 due to the delocalization of the lone pair of electrons on the N-atom into the benzene ring and less available for protonation. Pyrrole is not at all basic because the lone pair of electrons on N -atom is donated towards aromatic sextet formation. Therefore, pyrrolidine has a strong tendency to accept a proton and hence the strongest base.

11.

(c) Butanamine

Explanation: In the **Hoffmann bromamide reaction**, the amine formed has one carbon less than that present in the amide. RCONH₂ + Br₂ + 4NaOH \rightarrow RNH₂ + Na₂CO₃ + 2NaBr + 2H₂O

12.

(d) Phenol Explanation: Phenol

13.

(b) CH₃NH₂

Explanation:
$$\operatorname{CH}_3\operatorname{CONH}_2 + \operatorname{Br}_2 + 4\operatorname{NaOH} \xrightarrow{\Delta} \operatorname{CH}_3\operatorname{NH}_2 + 2\operatorname{NaBr} + \operatorname{Na}_2\operatorname{CO}_3 + 2\operatorname{H}_2\operatorname{O}_3 + \operatorname{CO}_3 + 2\operatorname{H}_2\operatorname{O}_3 + 2\operatorname{H}_2\operatorname{O}$$

14. **(a)** The mixture of o, p, and m nitroaniline:

Explanation: Mixture of ortho, meta, and para nitroaniline is formed because of the formation of anilinium ion which is formed by direct nitration of aniline.

15.

(b) LiAlH₄ in ether

Explanation:

Aryl nitro compound cannot be converted into amine using (lithium aluminium hydride) LiAlH₄ in ether.



16.

(b) p – aminoazobenzene

Explanation: This is a coupling reaction in which two benzene derivatives are held by -N=N- linkage resulting in the formation of an azo compound.

 $C_6H_5N_2^+Cl^- + C_6H_5NH_2 \rightarrow C_6H_5 N=N C_6H_4NH_2$

$$\underbrace{ \underbrace{ N}_{i} = N_{i} \underbrace{ CI_{i}^{-} + H_{i}^{-}}_{P-aminoazohenzene} NH_{2} \xrightarrow{} NH_{2}$$

17.

(b) diazonium chloride

Explanation: Aniline reacts with NaNO₂ and HCl to produce HNO₂ (nitrous acid). HNO₂ reacts with aniline at low temperature (273-278 k) to give benzene diazonium chloride which is stable.



18. **(a)** IV

Explanation: Hydrocarbon are more volatile than the amine.

19.

(b) 2 – butanamine

Explanation: Sec – Butylamine is the common name of 2-butanamine (CH₃CH₂CHNH₂CH₃).

20.

(b) Aluminium chloride reacts with Aniline

Explanation: AlCl₃ being a lewis acid reacts with the lone pair of $-NH_2$ group of aniline forming an adduct ($C_6H_5NH_2^+AlCl_3$) which deactivates the benzene system hence no friedal craft reaction occurs.

21.





Electron withdrawing group decreases the basic strength of aniline while electron releasing groups increases the basic strength of aniline.

22.

(b) Benzene diazonium chloride Explanation: Benzene diazonium chloride

23.

(d) major product is para nitroanisole

Explanation: In p-nitroanisole, the lone pair on oxygen is in conjugation with the pi bond of the benzene ring. Due to resonance, the nucleophilic centers are created at ortho and para positions. -OCH₃ hence is an activating group and hence o/p

activating. The NO_2^+ ion can attack at ortho and para positions, but since steric hindrance is least at para position, the major product is p-nitroanisole.

24. (a) m-nitroaniline

Explanation: In the presence of NH₄HS, one nitro group of dinitrobenzene gets reduced and gives m- nitroaniline as a major product.



(b) Dimethylamine

Explanation: NH₃ < primary amine < tertiary amine < secondary amine

This is because:

i. Steric hindrance

The size of an alkyl group is more than that of a hydrogen atom. So, an alkyl group would hinder the attack of a hydrogen atom, thus decreasing the basicity of the molecule. So, the more the number of alkyl groups attached, lesser will be its basicity.

ii. Solvation of ions

When amines are dissolved in water, they form protonated amines. Also, the number of possibilities for hydrogen bonding also increases. More the number of hydrogen bonding more is the hydration that is released in the process of the formation of hydrogen bonds.

26.

(d) Reaction with chloroform and alcoholic KOH

Explanation: Only primary amines react with CHCl₃ and alc. KOH to produce foul-smelling isocyanide. This test is known as Carbylamine Test (Hoffman's Isocyanide Test) for primary amines.

27. (a) N – nitrosoamines

Explanation:

Secondary amines react with nitrosonium ion to form N-nitrosoamine.

$$CH_{3}-NH-CH_{3} \xrightarrow{NaNO_{2}} (CH_{3})_{2}-N-N=O$$

$$N=O$$

$$N=O$$

$$N=O$$

$$CH_{3}$$

$$N=O$$

$$CH_{3}$$

$$CH_{3}$$

$$N-methylaniline$$

$$N-nitroso N-methylaniline$$

28.

(d) Friedal Craft Reaction

Explanation: The F.C. alkylation and F.C. acylation reaction take place in the presence of anhydrous AlCl₃, which is a Lewis base as it is electron deficient, it attacks the lone pair on nitrogen in aniline and forms an insoluble complex which precipitates out and reaction does not happen further.

 $C_6H_5NH_2 + AlCl_3 \rightarrow C_6H_5NH_2^+AlCl_3$

29.

(d) An alcohol

Explanation:

$$\underbrace{\bigcup_{\text{cold}}^{\text{NO}_2} \underbrace{\xrightarrow{4\text{NO}_2}_{\text{cold}}}_{\text{But, R-NH}_2 \underbrace{\xrightarrow{4\text{NO}_2}_{\text{cold}}}^{\text{NO}_2\text{Cl}^-} R-\underset{\text{alcohol}}{\text{oh}} + N_2 + H_2O$$

30.

(d) Ethanolic NaCN **Explanation:** KCN is used to increase the number of carbon atoms. $RX + NaCN \rightarrow RCN + KX$ $R - CN + 4H \xrightarrow{H_2/Raney Ni} RCH_2NH_2$

31.

(c) LiA/H₄

32.

(c) N-methylprop-2-en-1-amine

Explanation: IUPAC -
$$\overset{3}{\overset{0}{\operatorname{C}}}\operatorname{H}_{2} = \overset{2}{\overset{0}{\operatorname{C}}}\operatorname{H}^{1}_{\overset{0}{\operatorname{C}}}\operatorname{H}_{2} \overset{*}{\underset{CH_{3}}{\overset{|}{\operatorname{N-Methylprop-2-en-1-amine}}}}$$

33.

(b) HNO₃, H₂SO₄, 288K

Explanation: It is direct nitration of aniline using a nitrating mixture which gives a mixture of products. The optimum temperature required is 288K.

34. (a) Treatment of amide with bromine in an aqueous solution of sodium hydroxide
 Explanation: Aliphatic and aryl/alkyl primary amines can be prepared by the reduction of the corresponding nitriles with lithium aluminium hydride LiAIH₄.

$$\mathrm{R-C} \equiv \mathrm{N} \ \mathrm{Ar-C} \equiv \mathrm{N}
ightarrow \mathrm{LiAlH}_4 \ \mathrm{RCH}_2 \mathrm{NH}_2 \ \mathrm{Arynitrite} \ \mathrm{I}^{o_a \min e}$$

Heating alkyl halide with primary, secondary, and tertiary amine can be prepared by reduction of LiAlH₄ ether followed by

$$\mathrm{R-CONH_2} \xrightarrow{(i)LiAlH_4/ether} \mathrm{R-CH_2-NH_2} \ \xrightarrow{(ii)H_2O} \mathrm{R-CH_2-NH_2}$$

Heating alkyl halide with potassium salt of phthalimide followed by hydrolysis produces primary amine. This process is known as Gabriel's phthalimide reaction. The number of carbon atoms in the chain of amines of the product is the same as a reactant.



35. **(a)** 1° R-NH₂ + RCHO followed by H₂ /Pt

Explanation:
$$\underset{1^{o}Anime}{\text{R}-\text{NH}_{2}} + \underset{Aldehyde}{\text{O}=\text{HCR}} \xrightarrow[animation]{\text{Re} ductive}{\text{R-N=CHR}} \underset{\text{Re} duction}{\overset{H_{2}/Pt}{\text{R}-\text{NH}} \underset{\text{RoH}}{\text{RNH}} \underset{2^{o}Anime}{\text{RNH}} - \underset{2^{o}Anime}{\text{CH}_{2}\text{R}} (\text{secondary amine formed})$$

36.

(c) $C_6H_5CH_2Br$

Explanation:

SN1 substitution reaction occurs in two steps. In the first step, R-X bond is broken to produce a carbocation that is attacked by the nucleophile. The greater the stability of carbocation, the greater will be the rate of reaction. Benzylic halides show high reactivity towards S_N1 reaction.



37. (a) Benzene sulphonyl chloride

Explanation: Hinsberg's reagent which is used to test amines is benzene sulphonyl chloride.

38.

(d)
$$CH_3 - CH_2 - \overset{\circ}{\overset{\circ}{C}} - NH_2$$

Explanation: $CH_3 - CH_2 - \overset{\circ}{\overset{\circ}{C}} - NH_2$

39.

(d) 3

Explanation: Due to resonance, this position is electron rich and steric hindrance will be the least.

40. (a) HCOOH

Explanation: In carboxylic acids, the intermolecular hydrogen bonding is very strong compared to alcohols, therefore, it has the highest boiling point.

On the other hand, alcohols form stronger hydrogen bonds (intermolecular) compared to amines. And alkanes are non-polar so do not form any hydrogen bonds.

As the strength of hydrogen bonding increases, the boiling point also increases.

Thus boiling point order will be HCOOH > CH_3OH > CH_3NH_2 > CH_3CH_3 .

41.

(c) $NH_2^- > OH^- > NH_3 > H_2O$

Explanation: $NH_2^- > OH > NH_3 > H_2O$. Due to higher electronegativity of O than N atom, the O-H bond is more polar than the N-H bond. Hence, O-H is more acidic in nature than the N-H bond. Now, NH_2 and OH have a negative charge due to which they are more basic than NH_3 and H_2O .

42.

(**d**) CH₃CH₂NO₂

Explanation: A primary nitro compound on reduction will give primary amine. The reduction can be done using Fe/HCl or Sn/HCl.

43.

(c) Gabriel phthalimide synthesis

Explanation:

Gabriel phthalimide synthesis is used to get primary amine is prepared from alkyl halide without any change in the number of carbon atoms.



44.

(d) LiAlH₄ in ether

Explanation:

CH₃CHCONH₂ CH₃CHCH₂NH₂
+ 4H⁻
$$\xrightarrow{\text{LiAlH}_4}$$
 + H₂O
2-Phenylpropanamine

When 2-phenyl propanamide reacts with LiAlH₄ it undergoes reduction and produces amine.

45.

(b) Benzoic acid

Explanation: Benzoic acid reacts with NaOH to form sodium benzoate, this is a neutralization reaction where acid reacts with a base to give salt and water.

 $\rm C_6H_5COOH + NaOH \rightarrow C_6H_5COO^-Na^+ + H_2O$

46.

(b) CH₃NH₂

Explanation: Aliphatic primary amines react with nitrous acid (prepared in situ from NaNO₂ and a mineral acid such as HCl)

to form aliphatic diazonium salts, which is unstable and decomposes to give a carbocation and evolve N_2 gas. The carbocation so formed reacts with water from medium to give further produce alcohol.

47.

(d) Aniline

Explanation:

Azo-dye test is given by primary aromatic amines. Primary aromatic amines react with nitrous acid to form diazonium salt which undergoes a coupling reaction with beta-naphthol to give orange dye.



48.

(d) N-Ethyl-N-methylethanamine

Explanation: By alkylation reaction of methyl amine with two moles of ethyl chloride, N-Ethyl-N-methylethanamine is formed.

$$\begin{array}{c} \mathrm{CH}_{3}\mathrm{NH}_{2}+\mathrm{C}_{2}\mathrm{H}_{5}\mathrm{Cl} \longrightarrow \mathrm{CH}_{3}-\underset{|\\\mathrm{CH}_{2}\mathrm{CH}_{3}}{\mathrm{NH}_{3}} \xrightarrow{\mathrm{C}_{2}\mathrm{H}_{5}\mathrm{Cl}} & \mathrm{CH}_{3}-\underset{|\\\mathrm{CH}_{2}\mathrm{CH}_{3}}{\mathrm{C}_{2}\mathrm{H}_{5}} \\ & (\mathrm{N-ethyl-N-methylethanamine}) \end{array}$$

49.

(d) –N=N– bond and electrophilic substitution reaction

Explanation: Due to their positive charge, diazonium cations may participate in an electrophilic aromatic substitution as an electrophile. The electrophilic reaction center is the terminal nitrogen of the -N=N⁺group. As a result, two aromatic compounds are coupled by a -N=N- group. This is known as the azo group (diazo group). The corresponding reaction is called diazonium coupling (diazo coupling, azo coupling). However, the electrophilicity of diazonium ions is only relatively weak, as their positive charge is delocalized.

50.

(b)
$$O_2N \longrightarrow NH_2$$

Explanation: $O_2N \longrightarrow NH_2$ has highest value of pk_b

51.

(d) Triethylamine

Explanation:

Triethylamine (3⁰ amine) - replacement of 3 hydrogens by alkyl/aryl tertiary amine is formed.

52. (a) Br₂/NaOH

Explanation:
$$CH_3 - C_{|}H - CONH_2 \xrightarrow[(Hofmann's bromamide reaction)]{Hofmann's bromamide reaction)} CH_3 - C_{|}H - NH_2 + Na_2CO_3 + 2H_2O_{|}C_6H_5$$

2 - Phenylpropanamide 1 - Phenyletanamine

53. (a) Ethanamine

 $\begin{array}{c} \textbf{Explanation: } CH_3CH_2CONH_2 + Br_2 + 4NaOH \xrightarrow{\Delta} CH_3CH_2NH_2 + 2NaBr + Na_2CO_3 + 2H_2O \\ Propanamide \end{array}$

This is Hoffman Bromamide reaction.

54. **(a)** (CH₃)₂NH

Explanation: Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base. Thus, the order of the basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order. Further $C_6H_5NHCH_3$ is less basic than both $CH_3 NH_2$ and $(CH_3)_2NH$ due to the delocalization of the lone pair of electrons present on the nitrogen atom into the benzene ring.

55.

(b) water

Explanation: Amines are soluble in water due to hydrogen bonding with water.

56.

(c) Potassium phthalimide, $C_6H_4(CO)_2N^-K^+$

Explanation:

Potassium phthalimide is the source of nitrogen in Gabriel's phthalimide synthesis.



57.

58.

(c) Hoffmann bromamide reaction

Explanation: In Hoffmann bromamide degradation reaction, the amine formed has one carbon less than the amide. $RCONH_2 + Br_2 + 4NaOH \rightarrow RNH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

59.

(c) N-ethyl propan -1-amine

Explanation:

This is secondary amine because nitrogen is connected to 2 carbon atoms directly.



60. (a) Coupling reaction

Explanation: The reaction is known as Coupling reaction.

61.

(b) 2 – pentanamine

Explanation: 2-pentamine will have a chiral centre, therefore it can be resolved into enantiomers. CH₃CH₂CH₂C+HCH₃NH₂

The C* in 2-pentan amine is the chiral center.

(b) (CH₃)₂NH

Explanation: $(CH_3)_2NH$, because of +I effect of two alkyl group which increases electron density on nitrogen hence basicity increases compare to CH_3NH_2 which has only one alkyl group with +I effect.

In $C_6H_5NH_2$, lone pair on nitrogen is in resonance with the phenyl system hence lone pair availability on N of -NH₂ group decreases and basicity also decreases.

In case, $(C_6H_5)_2NH$, there are two phenyl rings attached to -NH group, the lone pair on N is engaged in resonance with two phenyl systems, and hence it is least basic.

63.

(d)
$$\sim$$
 NH₂
Explanation: \sim NH₂

64.

(c) p - nitroaniline < aniline < p - toluidine < p - methoxyaniline

Explanation: -OMe group at a para position will increase the basicity of more than- CH_3 group at the para position. While the presence of $-NO_2$ at a para position will decrease the basicity.

65. (a) Isobutyl amine

Explanation: Gabriel phthalimide synthesis cannot be used for preparation of aromatic amines, as aromatic halides do not undergo nucleophilic substitution by salt formed by phthalamide.

66.

(b) Nitrobenzene

Explanation: Diazonium cation is a weak electrophile and hence reacts with electron-rich compounds containing electrondonating groups such as -OH, -NH, and -OCH groups and not with compounds containing electron-withdrawing groups such as -NO₂, etc. Hence not react with nitrobenzene.

67.



Explanation:

Due to the delocalization of the lone pair of electrons on the N-atom into the benzene ring making it less available for protonation, $C_6H_5NH_2$ is the weakest base.

Resonating Structure of Aniline



68.

(b) N₂

Explanation:

The chemical reaction takes place during the reaction of methylamine with nitrous acid is as follows

$$CH_{3} - NH_{2} \xrightarrow{HNO_{2}} CH_{3} - N \equiv NCI^{-}$$

$$Methylamine \qquad \qquad \downarrow \Delta H_{2}O$$

$$CH_{3}OH + N_{2} \uparrow$$
Methanol

Explanation: The greater will be the strength of the base, the greater will be its reactivity towards dilute HCI. Hence, $(CH_3)_2NH$ secondary amine has the highest basic strength as it has the highest reactivity.

70.

(c) sp³ **Explanation:** Pyrrolidine is tetrahydropyrrole.



The nitrogen atom in pyrollidine is sp³ hybridized. Two sp³ hybridized orbitals are involved in pairing with carbon, one sp³ hybridized orbital is involved in pairing with hydrogen and one sp³ hybridized orbital is occupied by a lone pair.

71.

(d) N - ethyl - 1 - propanamine

Explanation: N of N – ethyl – 1 – propanamine is bonded to two carbon atoms, therefore it is a secondary amine.

72.

(c) a sulphonamide

Explanation: Sulphonyl chloride reacts with the primary amine to form sulphonamide.

 $RNH_2 + R^I SO_2 Cl \rightarrow R^I SO_2 NHR + HCl$

73.

(d) Aromatic primary amines

Explanation: In Gabriel's phthalimide reaction, the potassium salt of phthalimide is formed. It reacts readily with the primary alkyl halide to form the corresponding alkyl derivative. But aryl halide (C_6H_5X) does not react with potassium salt of

phthalimide. Because C-X bond in haloarene (alkyl halide) is difficult to be cleaved due to a partial double-bond character. Hence, do not undergo SN₂ reaction with potassium salt of phthalimide. So, aromatic primary amines cannot be prepared by Gabriel phthalimide synthesis.

74.

(b) 2 - bromo - N - methylaniline

Explanation: The **IUPAC** name of $\bigvee_{Br}^{NHCH_3}$ is **2-bromo-N - methylaniline.**

75.

(c) pyrrole

Explanation: This is pyrrole, a heterocyclic compound.