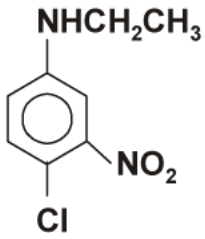
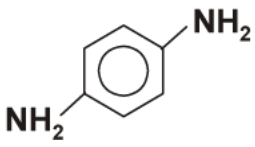
Date: 26/10/2021

Q1. Give the IUPAC names of the following compound.



Q2. Give the IUPAC names of the following compound.



Q3. Draw the structure of *p-tert-butylaniline* compound.

Q4. Draw the structure of *p-fluoroaniline* compound and give IUPAC name.

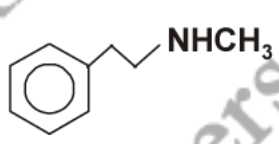
Q5. Draw the structure of *t-butylamine* compound and give IUPAC name.

Q6. Draw the structure of *N-isopropylaniline* compound and give IUPAC name.

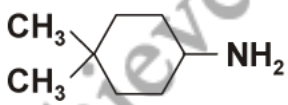
Q7. Draw the structure of *p-toluidine* compound and give IUPAC name.

Q8. Draw the structure of *N-Ethyl-4-isopropyl-N-methylaniline* compounds and give IUPAC name.

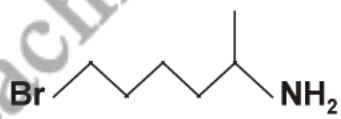
Q9. Give the IUPAC names of the following compound.



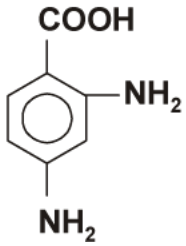
Q10. Give the IUPAC names of the following compound.



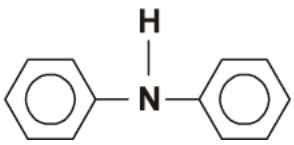
Q11. Give the IUPAC names of the following compound.



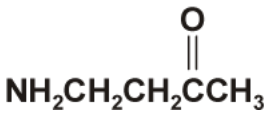
Q12. Give the IUPAC names of the following compound.



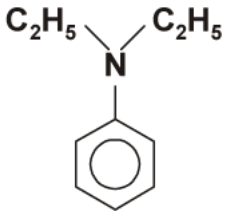
Q13. Give the IUPAC names of the following compound.



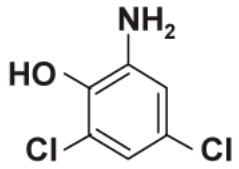
Q14. Give the IUPAC names of the following compound.



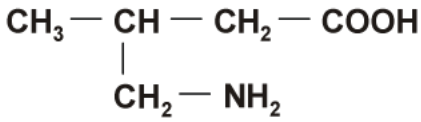
Q15. Give the IUPAC names of the following compound.



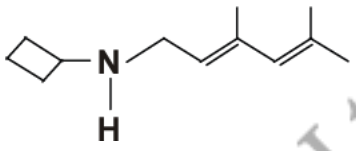
Q16. Give the IUPAC names of the following compound.



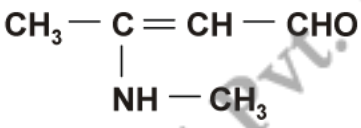
Q17. Give the IUPAC names of the following compound.



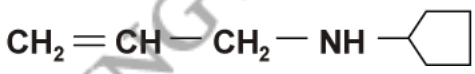
Q18. Give the IUPAC names of the following compound.



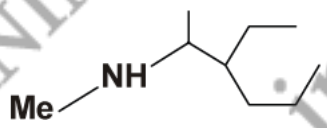
Q19. Give the IUPAC names of the following structure.



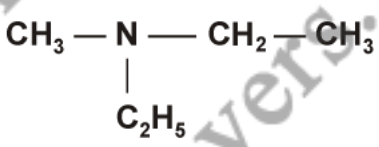
Q20. Give the IUPAC names of the following structure.



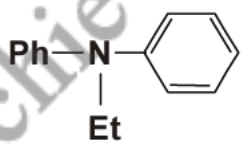
Q21. Give the IUPAC names of the following compound.



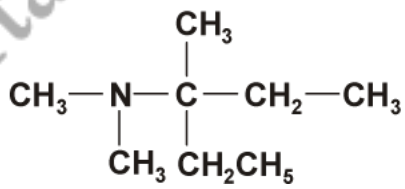
Q22. Write the IUPAC name of the following structure.



Q23. Give the IUPAC names of the following compound.

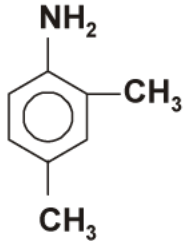


Q24. Give the IUPAC names of the following structure.

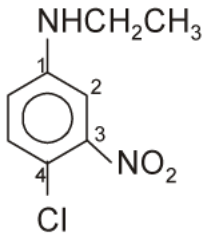


Q25. Give the IUPAC names of the following compound.

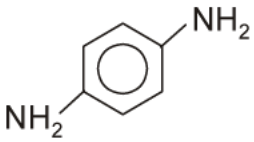
Q26. Give the IUPAC names of the following compound.



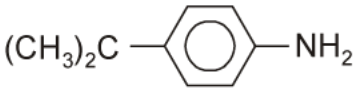
Date: 26/10/2021

S1. 

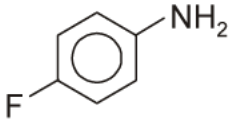
4-Chloro-3-nitro-N-ethyl aniline

S2. 

1, 4-Benzenediamine

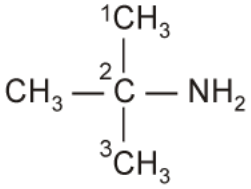
S3. 

p-tert-butylaniline

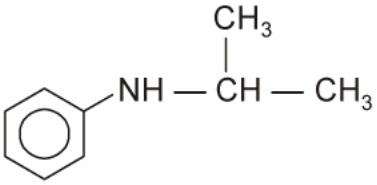
S4. 

P-Fluoroaniline (OR)

P-Fluorobenzenamine

S5. 

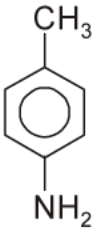
2-Methylpropan-2-amine

S6. 

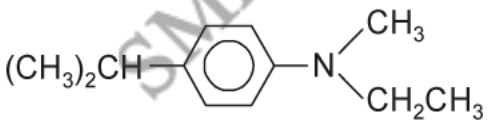
N-isopropyl benzenamine

(OR) *N*-Isopropyl-aniline

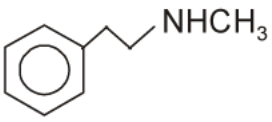
(OR) *N*-(Methylethyl) aniline

S7. 

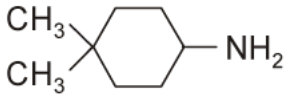
3 - Aminotoluene

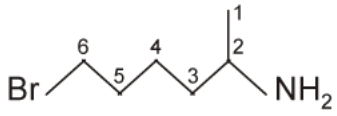
S8. 

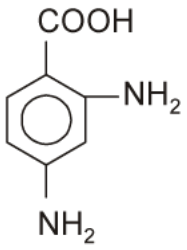
N-Ethyl-4-isopropyl-*N*-methylaniline

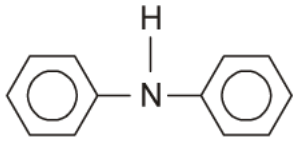
S9. 

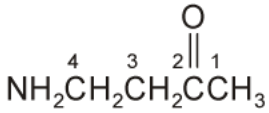
N-Methyl-2-phenylethanamine

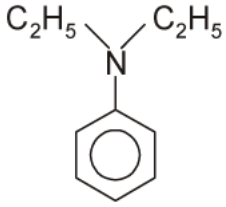
S10.  4, 4-Dimethlcyclohexanamine

S11.  6-Bromohexan-2-amine

S12.  2, 4-Diaminobenzoic acid

S13.  *N*-Phenylbenzenamine or *N*-Phenylaniline (Diphenylamine)

S14.  4-Aminobutan-2-one

S15.  *N*, *N*-Diethylbenzenamine (*N*, *N*-Diethylaniline)

S16. 4, 6-Dichloro-2-aminophenol.

S17. 4-Amino-3-Methylbutanoic acid

S18. *N*-Cyclobutyl-3,5-Dimethylhex-2,4-diene - 1 - amine

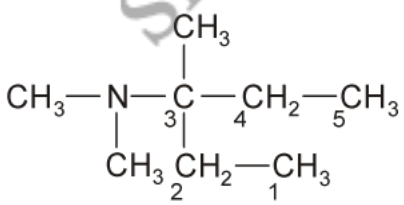
S19. *N*-Methyl-3-aminobut-2-enal.

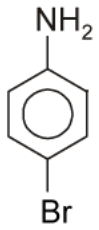
S20. *N*-Cyclopentylpropen-3-amine.

S21. 3-Ethyl-N-methylhexan-2-amine

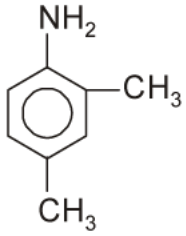
S22. *N*-Ethyl-*N*-methyl ethanamide.

S23. *N*-Ethyl-*N*-Phenylaniline (OR) *N*-Ethyl-*N*-Phenylbenzenamine.

S24.  3 Methyl *N*, *N*- d*i*-methylpentan - 3 - amine

S25. 

4 - Bromoaniline

S26. 

2, 4-Dimethylbenzenamine (2, 4-Dimethylaniline)

Date: 26/10/2021

Q1. Arrange the following in the decreasing order of their basic strength:
(a) $EtNH_2$ (b) $PhNH_2$ (c) NH_3 (d) $PhCH_2NH_2$

Q2. Arrange the following in the decreasing order of their basic strength:
(a) $PhNH_2$ (b) $EtNH_2$ (c) Et_2NH (d) NH_3

Q3. Arrange the following in the increasing order of solubility in water
$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

Q4. Give the decreasing order of boiling points of the following:
(a) EtOH (b) Me_2NH (c) $EtNH_2$

Q5. Give the decreasing order of solubility of the following in H_2O:
(a) $PhNH_2$ (b) Et_2NH (c) $EtNH_2$

Q6. Give the decreasing order of boiling points for the following:
(a) Me Me (b) Me OH (c) Me NH_2

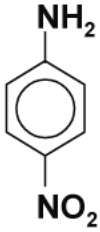
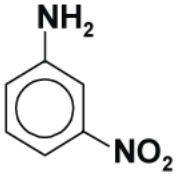
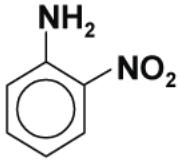
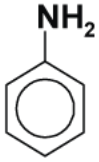
Q7. Give the decreasing order of boiling points for the following:
(a) Et_2NH (b) Me NH_2 (c) Et — N(Me)(Me)

Q8. Arrange the following in the decreasing order of their basic strength:
(a) $EtNH_2$ (b) Et_2NH (c) Et_3N (d) $PhNH_2$

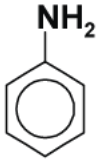
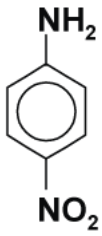
Q9. Arrange the following in the decreasing order of their basic strength:
(a) $MeNH_2$ (b) Me_2NH (c) Me_3N
(d) $PhNH_2$ (e) $PhCH_2NH_2$

Q10. Give the decreasing order of reactivity of diazonium ion coupling with phenol.
(a) *p*-NO_2 — $C_6H_4\overset{\oplus}{N}_2$ (b) *p*-Cl — $C_6H_4\overset{\oplus}{N}_2$ (c) $C_6H_5\overset{\oplus}{N}_2$
(d) *p*-Me — $C_6H_4\overset{\oplus}{N}_2$ (e) *p*-MeO — $C_6H_4\overset{\oplus}{N}_2$

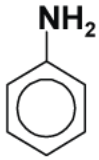
Q11. Give the decreasing order of reactivity of diazonium ion coupling with phenol.
(a) *p*-NO_2 — $C_6H_4\overset{\oplus}{N}_2$ (b) *m*-NO_2 — $C_6H_4\overset{\oplus}{N}_2$ (c) *p*-Cl — $C_6H_4\overset{\oplus}{N}_2$
(d) *m*-Cl — $C_6H_4\overset{\oplus}{N}_2$ (e) $Ph\overset{\oplus}{N}_2$

Q12. Arrange the following according to decreasing basic character.
(a)  (b)  (c)  (d) 

Q13. Arrange the following according to decreasing basic character.

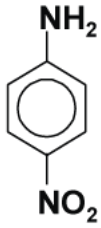
(a)  (b)  (c)  (d) 

Q14. Arrange the following according to decreasing basic character.


I

$(CH_3)_2NH$
II


III


IV

Q15. Arrange the following according to decreasing order of basic strength in gas phase

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

Q16. Arrange the following according to increasing order of basic strength

$C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$

Q17. Arrange the following according to increasing order of basic strength

Aniline, *p*-nitroaniline and *p*-toluidine

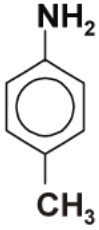
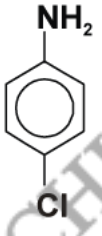
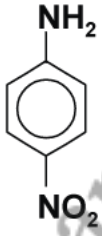
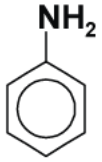
Q18. Arrange the following according to decreasing order of basic strength

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

Q19. Arrange the following according to decreasing order of the pK_b values

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

Q20. Arrange the following according to decreasing basic character.

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

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S1. (a) > (d) > (c) > (b).

S2. Aliphatic 2° amine > Aliphatic 1° amine > NH_3 > Aromatic amine

(c) > (b) > (d) > (a).

S3. Increasing order of solubility in water

$C_6H_5NH_2$ < $(C_2H_5)_2NH$ < $C_2H_5NH_2$.

S4. (b) > (a) > (c) > (alcohol > 1° > 2° amine).

S5. (a) > (c) > (b) (1° > 2° > amine > arylamine).

Arylamine is least soluble since it has a large hydrophobic part (phenyl group).

S6. (b) > (c) > (a) (alcohol > amine > alkane)

H-bonding in alcohol is stronger than in amine since the EN of O > N. Alkane does not from H-bonding.

S7. (b) > (a) > (c) (1° > 2° > 3° amine)

S8. (b) > (c) > (a) > (d)

S9. (b) > (a) > (c) > (e) > (d).

S10. (a) > (b) > (c) > (d) > (e)

Back up: (a) ⇒ (*p*-NO_2, –I and –R),
(b) ⇒ (*p*-Clm –I)
(c) ⇒ Standard,
(d) ⇒ (*p*-Me, +I and H.C.),
(e) ⇒ [*p*-MeO —, –I, and +R, net ED power of MeO — is greater than ED power of (Me —) group]

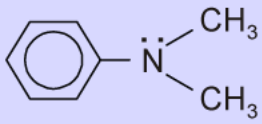
S11. (a) > (b) > (d) > (c) > (e)

Back up: (a) ⇒ (*p*-NO_2, –I, and –R),
(b) ⇒ (*m*-NO_2, only –I),
(d) ⇒ (*m*-Cl, –I, but –I at *m* > *p* and –I of NO_2 > –I of Cl).
(c) ⇒ (*p*-Cl —, –I),
(e) ⇒ Standard.

S12. (d) > (b) > (a) > (c).

Back up:	At ortho position – NO_2 show – M as well as – I effect (Ortho effect). At para position – NO_2 show – M effect. At Meta position – NO_2 show – I effect.

S13. (b) > (c) > (a) > (d).

Back up:  delocalization of lone pair nitrogen is very weak due to steric-hindrance  NO_2 has – M effect to.

S14. (II) > (III) > (I) > (IV).

S15. Decreasing order of basic strength in gas phase

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

S16. $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$.

S17. *p*-nitroaniline < aniline < *p*-toluidine.

S18. In decreasing order of basic strength

$(C_2H_5)_2NH > CH_3NH_2 > C_6H_5N(CH_3)_2 > C_6H_5NH_2$.

S19. In decreasing order of the pK_b values

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$.

S20. (a) > (d) > (b) > (c).

Back up:	CH_3	Produce + I effect
	Cl	Produce weak – I effect
	NO_2	Produce – M effect

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Q1. Although boron trifluoride adds on trimethylamine but it does not add on triphenylamine. Explain.

Q2. Methylamine in water reacts with ferric chloride to precipitate ferric hydroxide. Explain.

Q3. Can tertiary amines undergo acetylation reactions? Explain.

Q4. Why is it difficult to prepare pure amines by ammonolysis of alkyl halides?

Q5. Why is methylamine stronger base than ammonia?

Q6. Why does methylamine has lower boiling point than methanol?

Q7. Why are amines less acidic than alcohols of comparable molecular masses?

Q8. Suggest a structural formula of a compound having molecular formula $C_8H_{11}N$ (A) which is optically active, dissolves in dil. aqueous HCl and release N_2 with nitrous acid.

Q9. Aniline does not undergo Friedel Crafts alkylation. Explain.

Q10. Why do amines react as nucleophiles?

Q11. Account for the correct order of decreasing basicity of ethylamine, 2-aminoethanol and 3-amino-1-propanol.

Q12. Although trimethyl amine and *n*-propylamine have same molecular mass, the former boils at a lower temperature (276 K) than the latter (322 K). Why?

Q13. Why does silver chloride dissolve in methylamine solution?

Q14. Why diazonium salts of aromatic amines are more stable than those of aliphatic amines?

Q15. Tertiary butyl amine cannot be prepared by the action of NH_3 on tertiary butyl bromide. Explain.

Q16. For an amine RNH_2, write expression for K_b to indicate its base strength.

Q17. Although amino group is *o*- and *p*-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline. Explain.

Q18. Why do amines dissolve in mineral acids?

Q19. Why pK_b of aniline is more than that of methylamine.

Q20. Why ethylamine is soluble in water, whereas aniline is not?

Q21. Why are aliphatic amines stronger bases than aromatic amines?

Q22. Sulphanilic acid is soluble in di.NaOH but not in di.HCl. Explain.

Q23. Why does the reactivity of NH_2 get reduced in acetanilide?

Q24. Why does bromination of aniline, even under very mild conditions give 2, 3, 5-tribromoaniline instantaneously?

Q25. Account for the following order of increasing basicity:

$$\underset{\text{Nitrile}}{RC{\equiv}N} \quad < \quad \underset{\text{Imine}}{R'CH{=}NR} \quad < \quad \underset{\text{Amine}}{RNH_2}$$

Q26. Glycine exists as $NH_3^+CH_2COO^-$, zwitter ion but anthranilic acid (*p*-amino benzoic acid) does not exist as zwitter ion. Why?

Q27. Explain the observed K_b order for $Et_2NH > Et_3N > EtNH_2$ in aqueous solutions.

Q28. What will be the basic strength order of $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ in gas phase and compaire with aqueous state? Explain.

Q29. Which of the following is more basic in each set of species. Give reasons:
(a) Aniline and *p*-anisidine (b) Aniline and *m*-toluidine.

Q30. How do aromatic and aliphatic primary amines react with nitrous acid?

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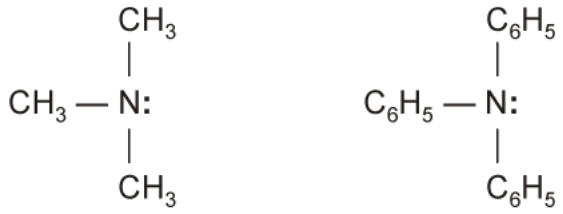
S1. Trimethylamine has three electron donating alkyl groups and therefore acts as a Lewis base and reacts with BF_3 (a Lewis acid).



Trimethylamine Triphenylamine

On the other hand, in triphenylamine, the lone pair of N gets delocalised over three benzene rings. Thus, the lone pair of not readily available to BF_3 for reaction.

S2. Mathylamine in water gives OH^- ions which react with ferric chloride to give the precipitate of ferric hydroxide as:

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3OH \rightleftharpoons CH_3NH_3^+ + OH^-$$

$$Fe^{3+} + 3OH^- \longrightarrow \underset{\text{Precipitate}}{Fe(OH)_3}$$

S3. No, tertiary amines cannot undergo acetylation reactions because these do not have replaceable hydrogen atom.

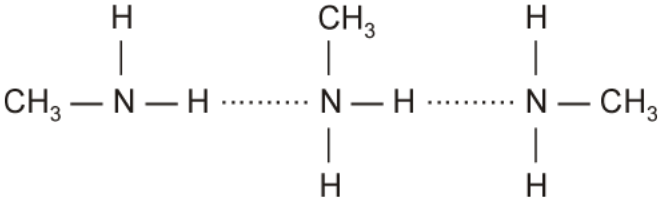
S4. By ammonolysis of alkyl halides, a mixture of primary, secondary and tertiary amines is formed

$$NH_3 \xrightarrow{RX} \underset{\text{1° Amine}}{R-NH_2} \xrightarrow{RX} \underset{\text{2° Amine}}{R_2NH} \xrightarrow{RX} \underset{\text{3° Amine}}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary salt}}{R_4N^+X^-}$$

The separation of these amines is very difficult. Thus, it is very difficult to prepare pure amines by ammonolysis of alkyl halides.

S5. Both ammonia and CH_3NH_2 have a lone pair of electrons and therefore, behave as Lewis bases. The alkyl group is CH_3NH_2 has + 1 inductive effect and is electron releasing in nature. As a result, its electron releasing tendency becomes more. Thus, CH_3NH_2 is more basic than ammonia.

S6. Methylamine is polar and can form intermolecular hydrogen bonds. However, its tendency to form intermolecular hydrogen bonds is less than that of methanol (CH_3OH), which has highly electronegative oxygen atom. As a result, CH_3NH_2 has lower boiling point than CH_3OH.



S7. Amines are less acidic than alcohols of comparable molecular masses because the anion formed is not stabilized enough due to presence of unshared electron pair on the nitrogen atom.

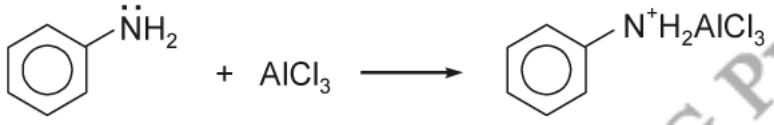
$$R-\ddot{N}H_2 \longrightarrow R\ddot{N}H^- + H^+$$

In another words, oxygen is more electronegative than nitrogen and its atom is smaller than that of nitrogen, as a result, it pulls the bonding electrons of the O — H bond towards itself, there by imparting acidic character to that alcoholic hydrogen. In case of amine, nitrogen-hydrogen bond is not much polar hence nitrogen atom tends to pick up a proton at its lone pair of electrons rather than push the hydrogen atom out as proton.

S8.

$$C_6H_5\underset{\displaystyle NH_2}{\underset{|}{C}}HCH_3$$

S9. Aniline does not undergo Friedel Craft alkylation reaction because of the formation of salt with aluminium chloride (Lewis acid) which is used as a catalyst. Due to this, nitrogen of aniline acquires positive charge and hence acts as a strong deactivating group for further reaction.



S10. Amines have a lone pair of electrons on N atom and therefore, react as nucleophiles.

S11. The correct order of decreasing basicity is:

$$CH_3CH_2NH_2 > HO(CH_2)_3NH_2 > HO(CH_2)_2NH_2.$$

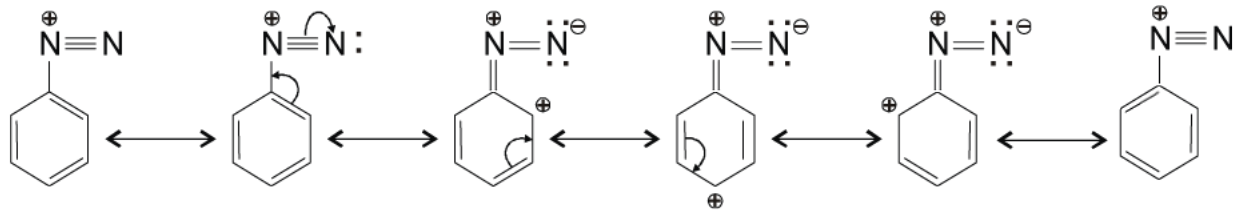
The electron withdrawing group – OH decreases the electron density on N, lowering its basicity. This effect decreases when distance from amino group increases

S12. *n*-Propylamine $CH_3CH_2CH_2NH_2$ has two hydrogen atoms on the nitrogen atom and therefore, forms intermolecular hydrogen bonding. Hence, its boiling point is high. On the other hand, trimethylamine, $(CH_3)_3N$ does not have hydrogen atom on the nitrogen atom. As a result, it does not undergo hydrogen bonding and hence its boiling point is low.

S13. Silver chloride dissolves in methylamine solution because it forms soluble complex.

$$CH_3NH_2 + AgCl \longrightarrow \underset{\text{Soluble complex}}{[Ag(CH_3NH_2)_2]^+Cl^-}$$

S14. Diazonium salts of aromatic amines are stabilized by resonance as the positive change of nitrogen atom is delocalised on benzene ring. Since this kind of stabilization is not possible in aliphatic amines, they are less stable than aromatic amines.



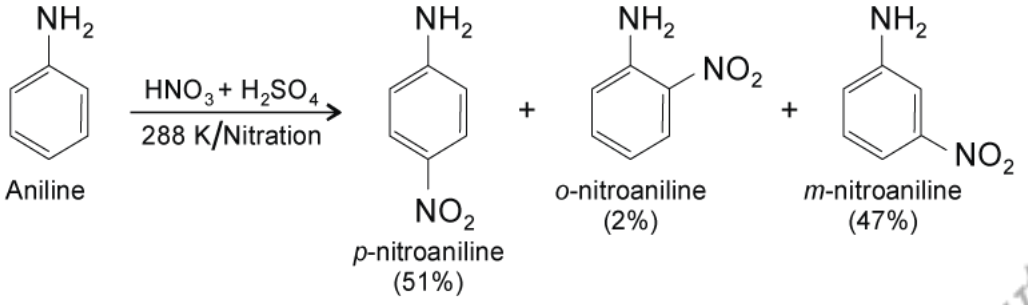
S15. Tertiary butyl bromide is a tertiary halide. On treatment with NH_3, the halide tends to undergo elimination giving alkene as the major product.

S16.

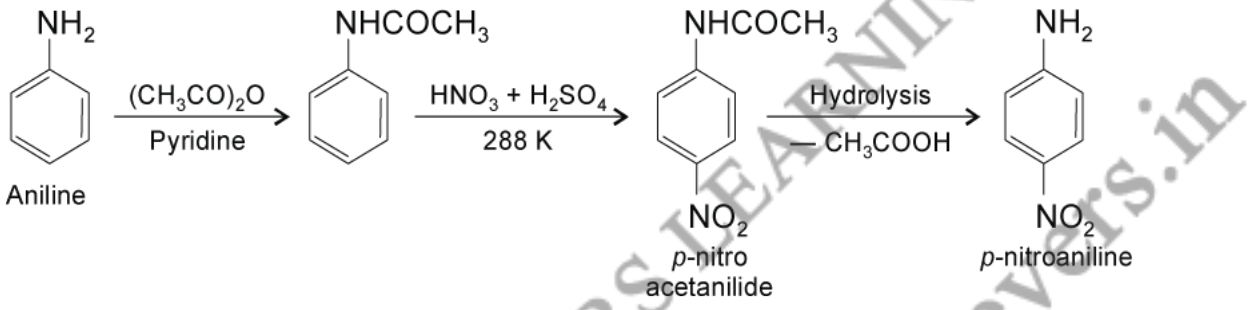
$$RNH_2 + H_2O \rightleftharpoons \overset{+}{R}NH_3 + OH^-$$

$$K_b = \frac{[\overset{+}{R}NH_3][OH^-]}{[RNH_2]}.$$

S17. In the presence of strong acids like sulphuric acid and nitric acid amino group becomes $-\overset{+}{N}H_3$ (Anilinium ion which is a *m*-directing group and hence in nitration product *m*-substitution is preferred.



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



S18. The nitrogen atom in amines contains a lone pair of electron which it can donate. Thus, they accept a proton from mineral acids to form a salt which is water soluble.

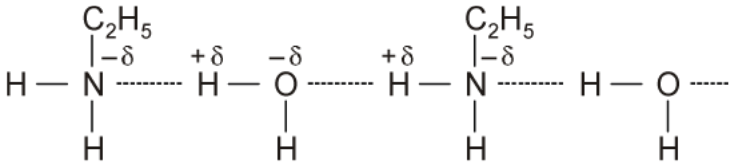
$$R-\ddot{N}H_2 + H^+Cl^- \longrightarrow [R-NH_3]^+Cl^-$$

Water soluble salt

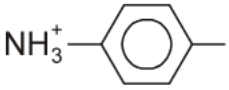
S19. Aniline has an electron withdrawing phenyl group on the nitrogen atom. It decreases electron density on nitrogen atom and makes it a weaker base. On the other hand, methyl group in methylamine is electron-donating group. It increases electron density on the nitrogen and makes it a stronger base.

Thus, methylamine is a stronger base than aniline and hence pK_b of aniline is more higher than that of methylamine.

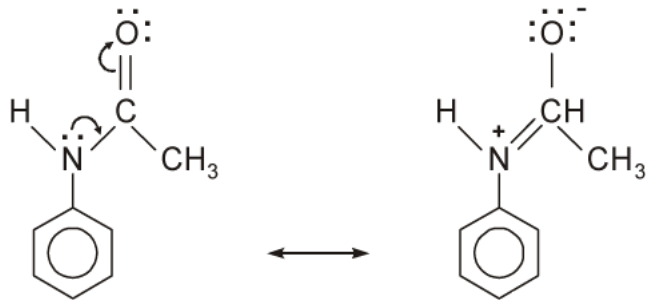
S20. Ethylamine is water soluble due to hydrogen bonding. However in aniline, the phenyl group is bulky in size and has – I effect. So aniline cannot formed hydrogen bonding with water.



S21. In aromatic amines have an electron withdrawing phenyl group on the nitrogen atom. It decreases electron density on nitrogen atom and makes it a weaker base than ammonia. In aliphatic amines alkyl group is electron donating and increases electron density on nitrogen thus making it a stronger base than ammonia. This is why alkyl amines are stronger bases than aromatic amines.

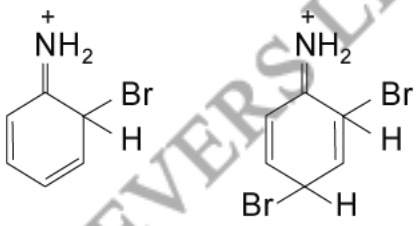
S22. Sulphanilic acid exists as a zwitter ion,  . In the presence of dil. NaOH, the weak. It acidic NH_3^+ group transfers its H^+ to OH^- to form a soluble *p*. $HN_2C_6H_4SO_3^-Na^+$. On the other hand, SO_3^- group is very weak base and therefore, does not accept a proton from dil. HCl to form *p*. $NH_3^+C_6H_4SO_3H$. Hence, it does not dissolve in dil.HCl.

S23. In acetanilide, the amide group withdraws electrons from NH_2 group as shown below:

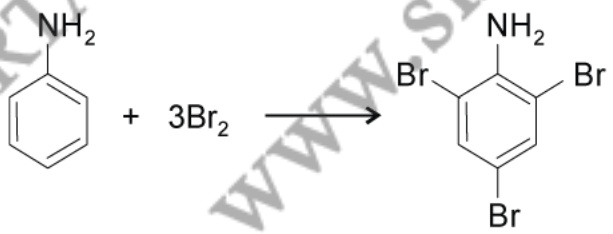


As a result, the electron pair on nitrogen gets displaced to the carboxyl group. Therefore, the unshared pair of electrons on nitrogen is less available for donation to the aromatic ring. Consequently, the density at *ortho* and *para* position in the benzene ring gets reduced which in turn results in reduced reactivity towards electrophilic substitution of benzene.

S24. The interaction of unshared electron pair on N with positive charged ring forming following structures. — NH_2 group of aniline greatly activates the benzene ring, because



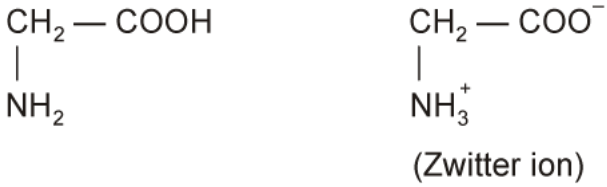
of which the electron density at *ortho* and *para* position increase appreciable. Thus, under very mild condition aniline instantaneously gets brominated at both position (*o*, *p*) to give white precipitate.



2, 4, 6-tribromo aniline
(While ppt.)

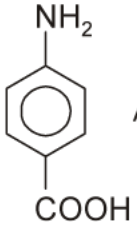
S25. In RC ≡ N, the N atom is *sp* hybridised, in R′CH = NR, the N atom is sp^2 hybridised while in RNH_2, the N-atom is sp^3 hybridised. The more *s*-character in the hybrid orbital of N with the lone pair of electrons, greater will be its tendency to be strongly held by the nucleus. Therefore, it will have lesser tendency to donate its electron pair and hence will behave as weak base. Thus, as *s*-character decreases from RCN, to RCH = NR to RNH_2 its basic character increases.

S26. Glycine exists as zwitter ion because the acidic group — COOH donates proton to basic — NH_2 group as:



(Zwitter ion)

However, in anthranilic acid, the electron withdrawing benzene ring suppresses the tendency of a weak acidic group (— COOH) to transfer its proton to — NH_2 group.



Anthranilic acid

S27. The value of K_b of a alkyl amine is determined by two factor (i) induction and (ii) solvation. Inductively, the alkyl groups, being electron releasing, increase the electron density on the nitrogen making the amine more basic (larger K_b). Increasing the number of alkyl groups should increase the basic character. In terms of solvation the basic character of an amine depends on ease of formation of its ammonium cation by accepting a proton. The more the number of hydrogen-atoms in the ammonium ion, the more it is stabilised by hydrogen-bonding. As alkyl groups replace hydrogen-atoms, hydrogen-bonding decreases and basic character of amine should decrease.

Thus, induction and solvation operate in opposite directions and three is a discontinuity in K_b values. Induction makes all the three alkyl amines stronger bases than ammonia. Thus, $(C_2H_5)_2NH$ is stronger than $C_2H_5NH_2$. However, when the third alkyl group is added, the basic character does not enhance and the opposing solvation effect assumes more importance. Thus, the order is

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

S28. The availability of lone pair electron in nitrogen of amine, which depends upon + I (inductive) effect of attached alkyl groups with nitrogen. Ease with which the proton of water can reach to the lone pair of electron on nitrogen, which depends upon the steric effect of the alkyl groups present on nitrogen of amine. So in gaseous state second factor (solvent effect) is absent hence the + I effect of alkyl group (which depends upon the number of alkyl groups and type of alkyl groups) will be the deciding factor. Thus, the order of basic strength of different ethyl amines will be:

In gas phase: $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2$

In aqueous state: $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2$

S29. (a) — $\ddot{O}CH_3$ group has strong + R effect, however it does have weak – I effect. But dominance of + R effect cause *p*-anisidine to become stronger base as compared to aniline.

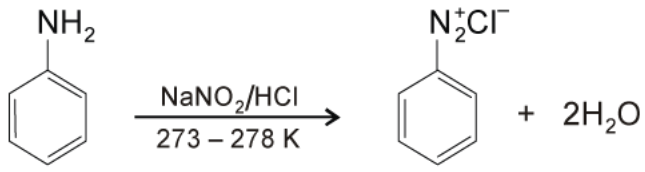
(b) *m*-toluidine is more stronger base than aniline because of electron releasing effect of CH_3 — group.

S30. (a) Primary aliphatic amines react with nitrous acid to form aliphatic diazonium salts which being unstable, liberate nitrogen gas quantitatively and predominently alcohols. Quantitative evolution of nitrogen is used in estimation of amino acids and proteins.

$$R — NH_2 + HNO_2 \xrightarrow{NaNO_2/HCL} [R — \overset{+}{N_2}\overset{-}{Cl}] \xrightarrow{H_2O} ROH + N_2 + HCl$$

$$CH_3NH_2 + HNO_2 \xrightarrow[273 - 278\ K]{NaNO_2/HCL} CH_3\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{H_2O} CH_3OH + N_2 + HCl$$

(b) Aromatic amines react with nitrous acid at low temperature (273 – 278 K) to form diazonium salts, a very important class of compounds used for synthesis of a variety of aromatic compounds.



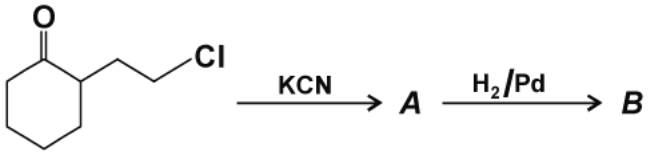
Aniline — Benzene diazonium chloride

Date: 26/10/2021

Q1. Write short notes on the diazotisation.

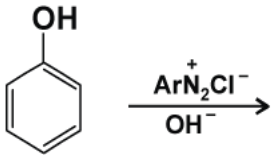
Q2. Write short notes on the carbylamine reaction.

Q3. Identify *A* and *B* in the following reaction.



Q4. Why is aniline soluble in aqueous HCl?

Q5. Complete the following reaction.



Q6. Complete the following reactions: $C_6H_5NH_2 + Br_2(aq) \longrightarrow$

Q7. Complete the following reactions: $C_6H_5N_2Cl + C_2H_5OH \longrightarrow$

Q8. Complete the following reactions: $C_6H_5NH_2 + H_2SO_4(conc.) \longrightarrow$

Q9. Complete the following reactions: $C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow$

Q10. Complete the following reactions: $C_6H_5NH_2 + CHCl_3 + alc.\ KOH \longrightarrow$

Q11. Write short notes on the coupling reaction.

O12. Write short notes on the Hoffmann's bromamide reaction.

Q13. Complete the following reactions: $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow$

Q14. Complete and name the following reactions:

(a) $RNH_2 + CHCl_3 + 2KOH \longrightarrow$ (b) $RCONH_2 + Br_2 + 4NaOH \longrightarrow$

Q15. Identify (A), (B) and (C) in $CH_3CH_2OH \xrightarrow{KMnO_4} A \xrightarrow[(ii)\ NH_3]{(i)\ SOCl_2} B \xrightarrow[NaOH]{Br_2} C$

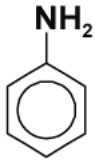
Q16. Identify (A), (B) and (C) in $CH_3CH(CH_3)-CONH_2 \xrightarrow{Br_2, NaOH} A \xrightarrow{HONO} B \xrightarrow{O} C$

Q17. Identify (A), (B) and (C) in $C_6H_5COOH \xrightarrow{PCl_5} A \xrightarrow{NH_3} B \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2, Ni} C$

Q18. An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compound A, B and C.

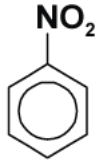
Q19. Write short notes on the Gabriel phathalamide synthesis.

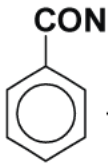
Q20. Complete the given reactions:

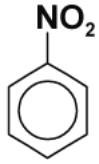
(a)  $\xrightarrow{(CH_3CO)_2O}$ A $\xrightarrow{Br_2}$ B $\xrightarrow{H^+, H_2O}$ C

(b) $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow[H^+]{NH_2OH}$ D $\xrightarrow{LiAlH_4}$ E

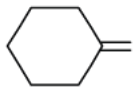
Q21. Write the formula of A and B in the following

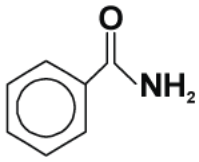
(a)  $\xrightarrow{Fe/HCl}$ A $\xrightarrow{CH_2-\overset{O}{\overset{\|}{C}}-Cl}$ B

(b)  $\xrightarrow{Br_2/KOH}$ A $\xrightarrow{C_6H_5COCl}$ B

(c)  $\xrightarrow{H_2/Pd}$ A $\xrightarrow{CHCl_3/KOH}$ B

Q22. Complete the given reactions:

(a)  $\xrightarrow{NH_3}$ F $\xrightarrow{Ni, H_2}$ G

(b)  $\xrightarrow{KOH, Br_2}$ H $\xrightarrow{CHCl_3, KOH}$ I

Q23. Give the structures of A, B and C in the following reactions

(a) $CH_3CH_2I \xrightarrow{NaCN}$ A $\xrightarrow[\text{Partial hydrolysis}]{OH^-}$ B $\xrightarrow{NaOH + Br_2}$ C

(b) $C_6H_5NO_2 \xrightarrow{Fe/HCl}$ A $\xrightarrow[273\ K]{NaNO_2 + HCl}$ B $\xrightarrow[\Delta]{H_2O/H^+}$ C

Q24. Give the structures of A, B and C in the following reaction:

(a) $C_2H_5\overset{+}{N}_2\overset{-}{Cl} \xrightarrow{CuCN}$ A $\xrightarrow{H_2O/H^+}$ B $\xrightarrow[Heat]{NH_3}$ C

(b) $CH_3CH_2Br \xrightarrow{KCN}$ A $\xrightarrow{LiAlH_4}$ B $\xrightarrow[0\ °C]{HNO_2}$ C

Q25. Give the structures of A, B and C in the following reaction:

(a) $CH_3COOH \xrightarrow[Heat]{NH_3}$ A $\xrightarrow{NaOBr}$ B $\xrightarrow{NaNO_2/HCl}$ C

(b) $C_6H_5NO_2 \xrightarrow{Fe/HCl}$ A $\xrightarrow[273\ K]{HNO_3}$ B $\xrightarrow{C_6H_5OH}$ C

Q26. An organic compound $C_8H_4O_3$, in dry benzene, in the presence of anhydrous $AlCl_3$ gives B. The compound B on treatment with PCL_5, followed by reaction with H_2/Pd ($BaSO_4$) gives compound E ($C_{14}H_{10}N_2$). Identify A, B, C and D. Explain the formation of D from C.

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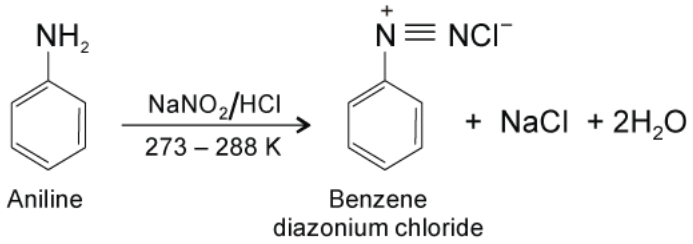
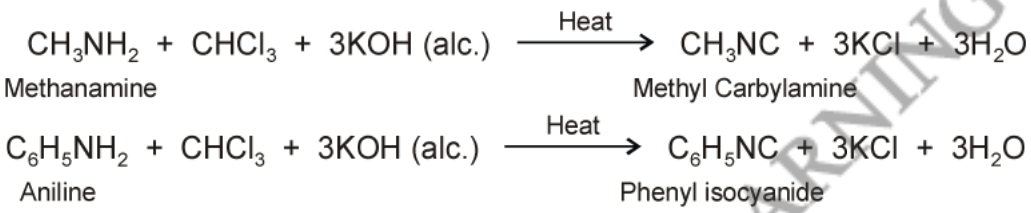
S1. Aromatic amines react with nitrous acid (HNO_2) at low temperatures (273 – 278 K) to form diazonium salts. The process is known as diazotisation.

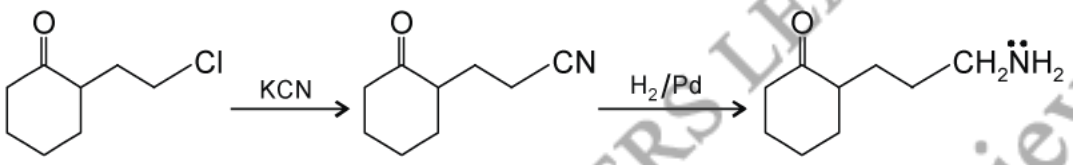


Diazonium salts are very important for the synthesis of various aromatic compounds.

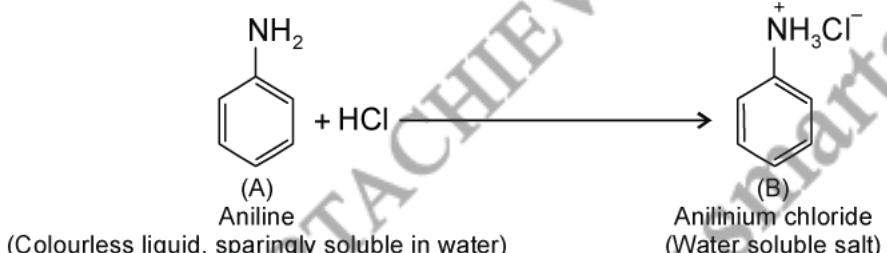
S2. Primary amines (both aliphatic and aromatic) when heated with chloroform and alcoholic potassium hydroxide form isocyanides (also known as carbylamines) which have a foul smell. This reaction is also known as isocyanide test and is used as a test for primary amines. Secondary and tertiary amines do not show this reaction.



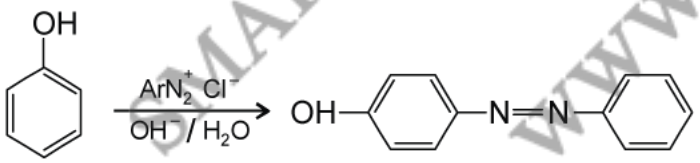
S3.



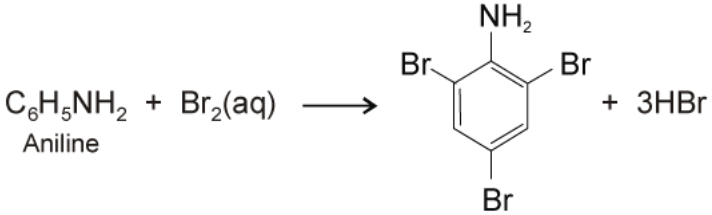
S4. Aniline forms the salt anilinium chloride with HCl which is water soluble.



S5.



S6.



S7. $C_6H_5\overset{+}{N}_2\bar{Cl} + C_2H_5OH \longrightarrow C_6H_5 + N_2\uparrow + H_2O + C_2H_5Cl$

Benzene-diazonium Chloride — Ethanol — Benzene — Chloroethene

S8. $C_6H_5NH_2 + \text{Conc. } H_2SO_4 \longrightarrow C_6H_5\overset{+}{N}H_3HSO_4^-$

Aniline — Anilinium hydrogen sulphate

S9. $C_6H_5\overset{+}{N}_2\bar{Cl} + H_3PO_2 + H_2O \longrightarrow C_6H_6 + H_3PO_3 + N_2 + HCl$

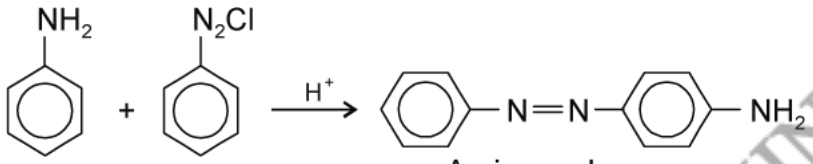
Benzene-diazonium Chloride — Benzene

S10. $C_6H_5NH_2 + CHCl_3 + \text{alc. KOH} \longrightarrow C_6H_5NC + 3KCl + 3H_2O$

Aniline — Chloroform — Phenyl isocyanide

S11. Diazonium salts react with phenols and aniline to give azo compounds which have an extended conjugate system having both the aromatic rings joined by — N ═ N — bond.

This is an example of electrophilic substitution reaction.



p-Aminoazobenzene

(Yellow dye)

S12. This is a method for the preparation of primary amines by treating an amide with bromine and alcoholic solution of sodium hydroxide.

$$R-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4NaOH(alc.) \longrightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

S13. $C_6H_5NH_2 + (CH_3CO)_2O \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$

Aniline — Acetic anhydride — Acetanilide — Acetic acid

S14. (a) $RNH_2 + CHCl_3 + 2KOH \longrightarrow RNC + 3KCl + 3H_2O$

The reaction is carbylamine reaction

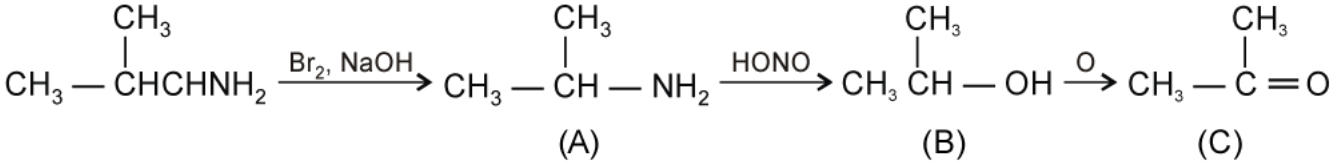
(b) $RCONH_2 + Br_2 + 4NaOH \longrightarrow RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O$

It is called Hoffmann bromamide degradation reaction

S15. $CH_3CH_2OH \xrightarrow{KMnO_4} CH_3COOH \xrightarrow[(ii)\ NH_3]{(i)\ SOCl_2} CH_3CONH_2 \xrightarrow[NaOH]{Br_2} CH_3NH_2$

(A) (B) (C)

S16.

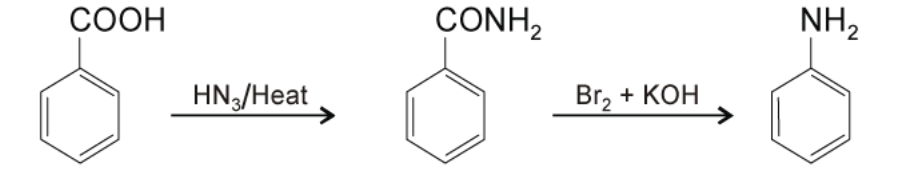


(A) (B) (C)

S17. $C_6H_5COOH \xrightarrow{PCl_5} C_6H_5COCl \xrightarrow{NH_3} C_6H_5CONH_2 \xrightarrow{P_2O_5} C_6H_5CN \xrightarrow{H_2, Ni} C_6H_5CH_2NH_2$

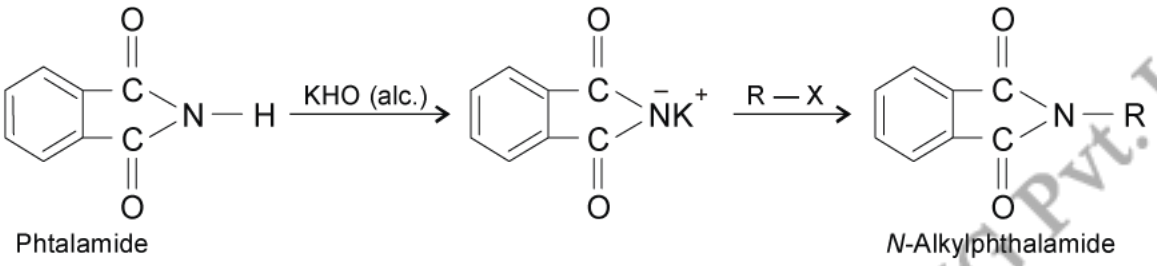
(A) (B) (C)

S18.

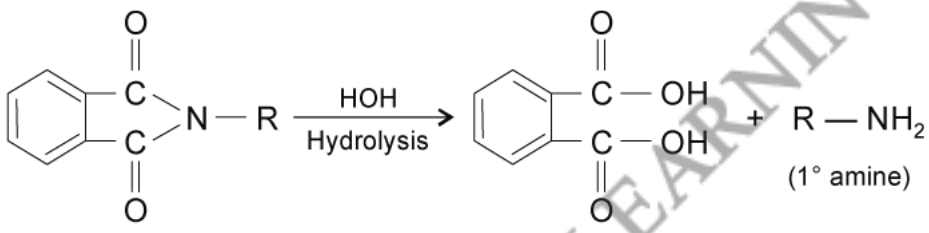


Benzoic acid Benzamide Aniline (C_6H_7N)

S19. Gabriel synthesis is used for the preparation of primary amines. Phthalamide on treatment with alcoholic potassium hydroxide forms potassium salt of phthalamide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine. Aromatic primary amines cannot be prepared by this method, because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalamide.



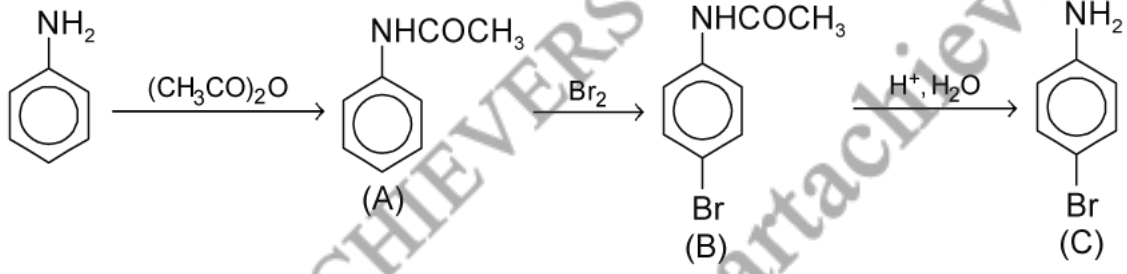
Phtalamide *N*-Alkylphthalamide



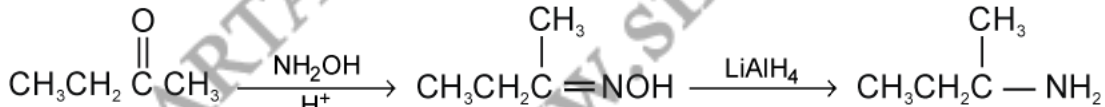
N-Alkylphthalamide Phthalic acid Alkylamine

S20.

(a)

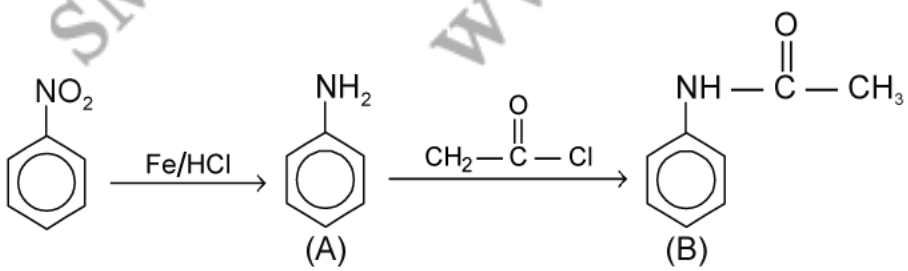


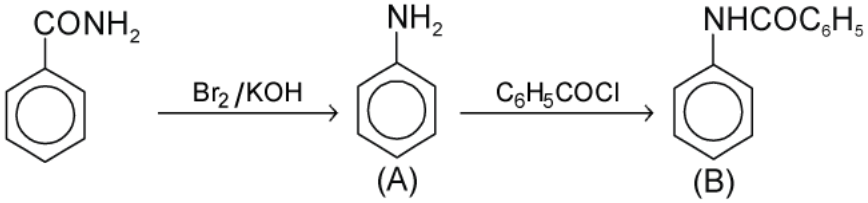
(b)

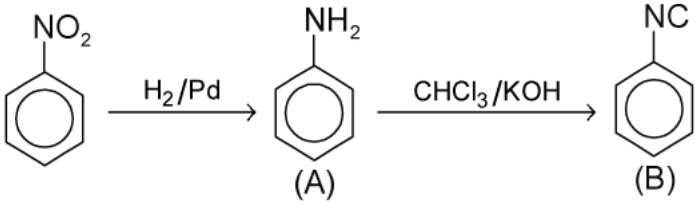


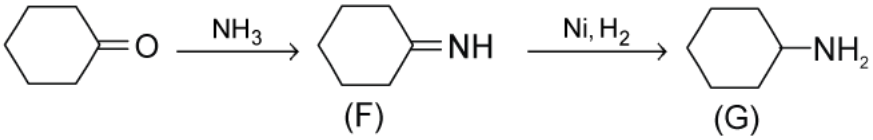
S21.

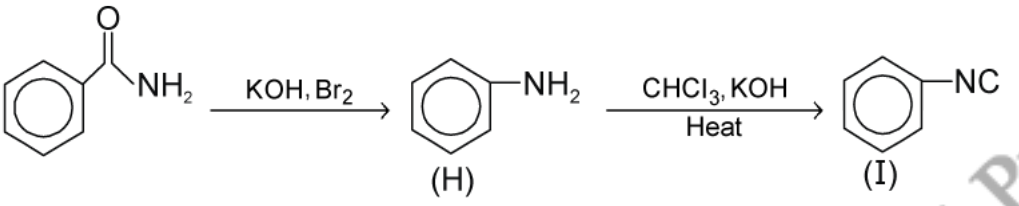
(a)



(b) 

(c) 

S22. (a) 

(b) 

S23.

(a) $CH_3CH_2I \xrightarrow{NaCN} \underset{\text{Propane nitrile (A)}}{CH_3CH_2CN} \xrightarrow[\text{Partial hydrolysis}]{OH^-} \underset{\text{Ethanamide (B)}}{CH_3-\overset{\overset{O}{\|}}{C}-NH_2} \xrightarrow[\text{Hoffmann bromamide reaction}]{NaOH + Br_2} \underset{\text{Methanamine (C)}}{CH_3NH_2}$

(b) $C_6H_5NO_2 \xrightarrow[\text{Reduction}]{Fe/HCl} \underset{\text{Aniline (A)}}{C_6H_5NH_2} \xrightarrow[273\ K]{NaNO_2 + HCl} \underset{\text{Benzene diazonium chloride (B)}}{C_6H_5N_2^+Cl^-} \xrightarrow{H^+, H_2O} \underset{\text{Phenol (C)}}{C_6H_5OH}$

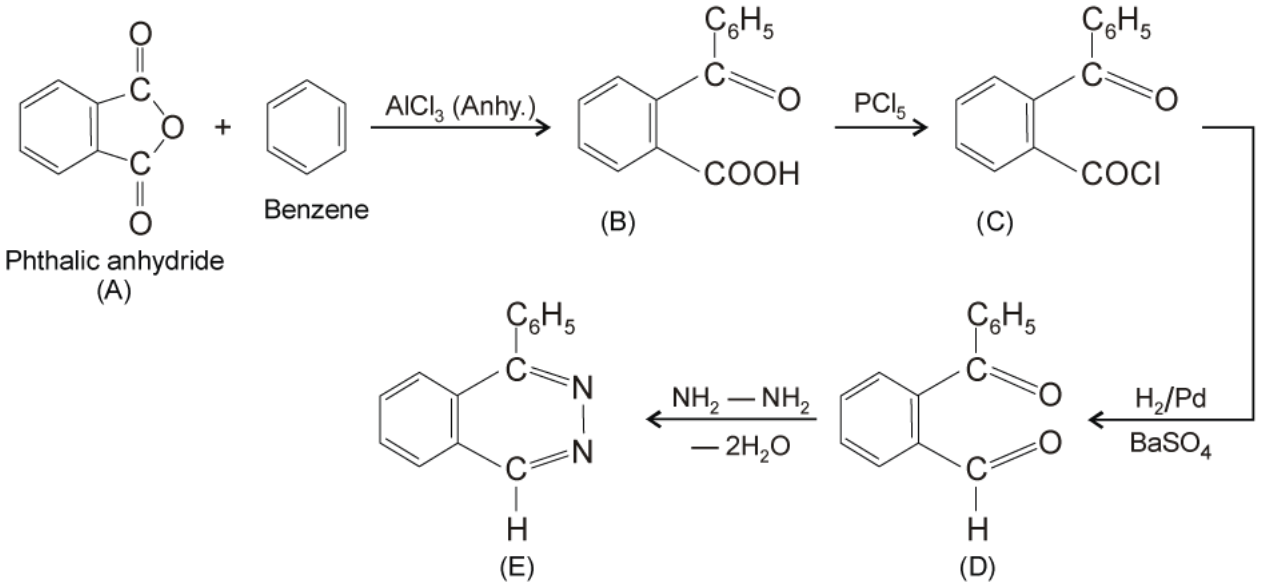
S24. (a) $\underset{\text{Benzenediazonium chloride}}{C_2H_5\overset{+}{N}_2\overset{-}{Cl}} \xrightarrow{CuCN} \underset{\text{Benzene nitrile}}{C_6H_5CN} \xrightarrow{H_2O/H^+} \underset{\text{Benzoic acid}}{C_6H_5COOH} \xrightarrow[Heat]{NH_3} \underset{\text{Benzamide}}{C_6H_5CONH_2}$

(b) $\underset{\text{Bromoethane}}{CH_3CH_2Br} \xrightarrow{KCN} \underset{\text{Propanenitrile}}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{Propanamine}}{CH_3CH_2CH_2NH_2} \xrightarrow[0\ ^\circ C]{HNO_2} \underset{\text{Propanol}}{CH_3CH_2CH_2OH}$

S25. (a) $\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[Heat]{NH_3} \underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow{NaOBr} \underset{\text{Methanamine}}{CH_3NH_2} \xrightarrow{NaNO_2/HCl} \underset{\text{Methanol}}{CH_3OH}$

(b) $\underset{\text{Nitrobenzene}}{C_6H_5NO_2} \xrightarrow[\text{Reduction}]{Fe/HCl} \underset{\text{Aniline}}{C_6H_5NH_2} \xrightarrow[273-278\ K]{HNO_3} \underset{\text{Benzenediazonium chloride}}{C_6H_5N_2^+Cl^-} \xrightarrow{C_6H_5OH} \underset{\text{p-hydroxyazobenzene}}{HO-C_6H_4-N=N-C_6H_5}$

S26.



Date: 26/10/2021

Q1. Write the conversion of aniline to *p*-bromoaniline.

Q2. Write the conversion of benzaminde to toluene.

Q3. Write the conversion of benzyl chloride to 2-phenylethanamine.

Q4. Write the conversion of acetanilide $\longrightarrow$ *p*-nitroaniline.

Q5. Write the chemical reaction equation to conversion of chlorobenzene from aniline.

Q6. Write the chemical reaction equation stating the reaction conditions required of the following conversion of aniline to phenol.

Q7. How will you convert benzyl chloride to 2-phenylethanamine?

Q8. How will you convert aniline to *p*-bromoaniline?

Q9. How will you convert benzoic acid to aniline?

Q10. How will you convert benzene to *m*-bromophenol?

Q11. How will you convert nitrobenzene to benzoic acid?

Q12. How will you convert chlorobenzene to *p*-chloroaniline?

Q13. How will you convert aniline to 2, 4, 6-tribromofluorobenzene?

Q14. How will you convert propanoic acid into ethanoic acid?

Q15. How will you convert nitromethane into dimethylamine?

Q16. How will you convert methanamine into ethanamine?

Q17. How will you convert ethanoic acid into propanoic acid?

Q18. How will you convert ethanamine into methanamine?

Q19. How will you convert methanol to ethanoic acid?

Q20. How will you convert hexanenitrile into 1-aminopentane?

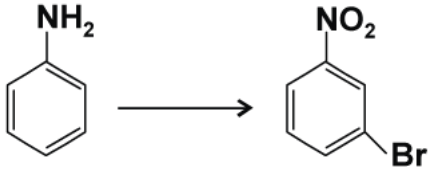
Q21. How will you convert ethanoic acid into methanamine?

Q22. How will you convert *P*-toluidine to 3, 5-dibromotoluene?

Q23. How will you convert aniline to benzyl alcohol?

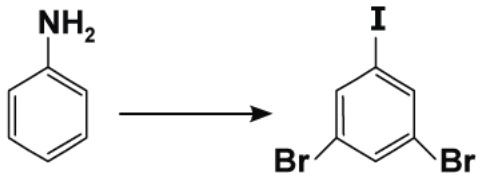
Q24. How will you convert from benzamide to toluene?

Q25. How will you carry out the following conversion?



Q26. Write the conversion of chlorobenzene to *p*-chloroaniline.

Q27. How will you carry out the following conversion?

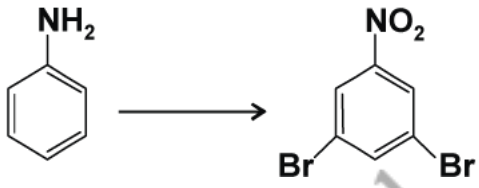


Q28. Write the chemical reaction equations stating the reaction conditions required for each of the following conversions:

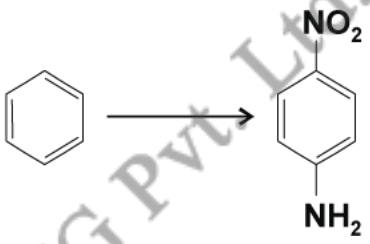
(a) Methyl bromide to ethyl amine (b) *p*-Toluidine to 2-bromo-4-methylaniline

(c) Acetaldehyde to ethylamine

Q29. How will you carry out the given below conversion?



Q30. How will you carry out the given below converstion?



Q31. How to convert Benzene to *m*-nitrophenol?

Q32. How to convert Toluene to *p*-toluic acid?

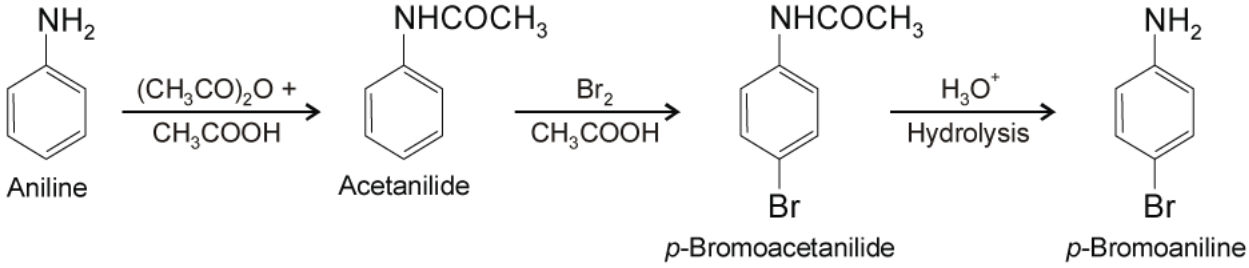
Q33. Write chemical equations for the following conversions:

(a) $C_6H_5CH_2NH_2$ into $C_6H_5CH_2OH$ (b) C_2H_5Cl into $(C_2H_5)_3N$

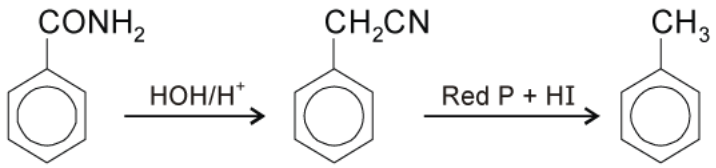
(c) Propene into butylamine

Date: 26/10/2021

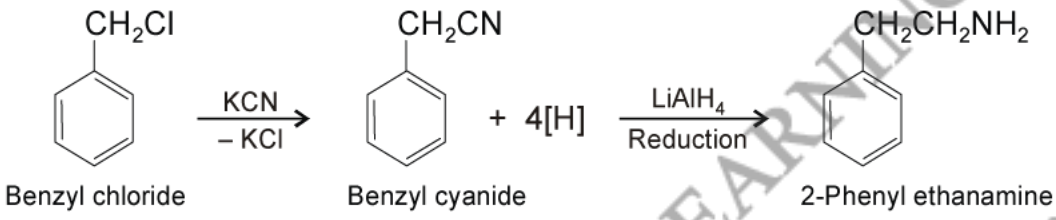
S1. Aniline to *p*-bromoaniline:



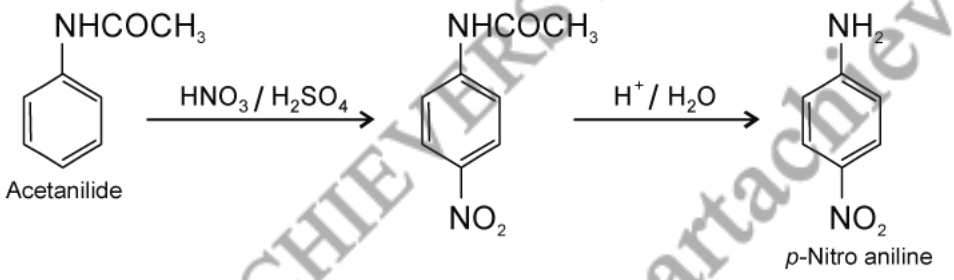
S2. Benzaminde to toluene:



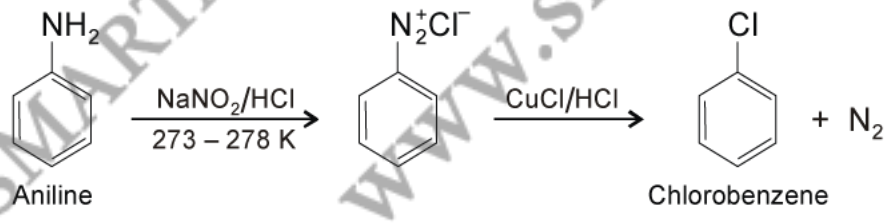
S3. Benzyl chloride to 2-phenylethanamine:



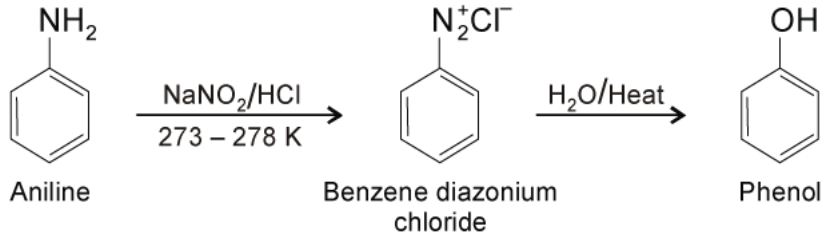
S4. Acetanilide ⟶ *p*-nitroaniline:



S5. Chlorobenzene from aniline:



S6. Aniline to phenol:



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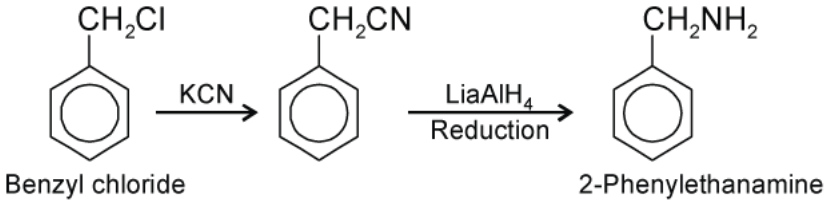

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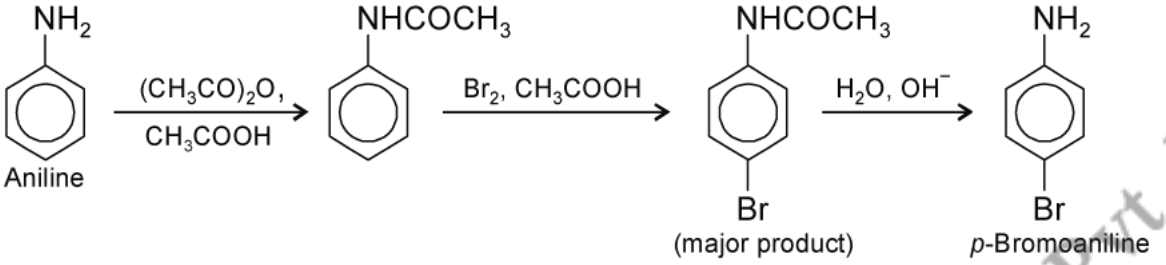

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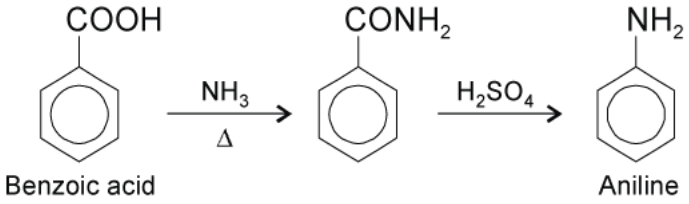

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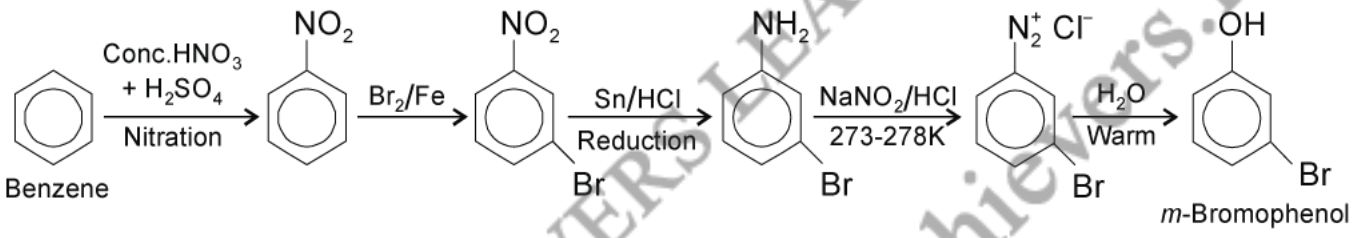

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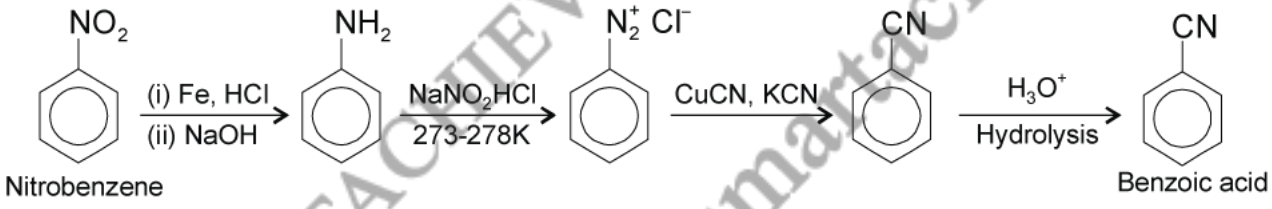

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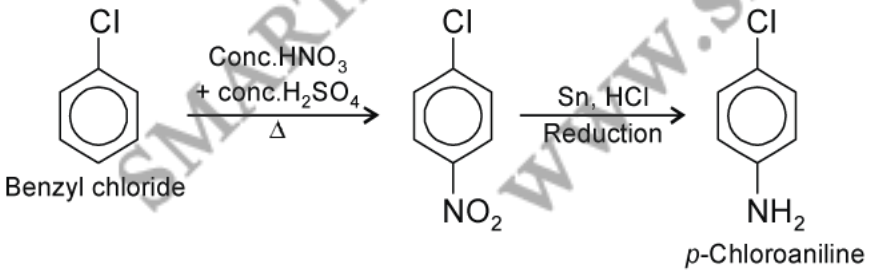

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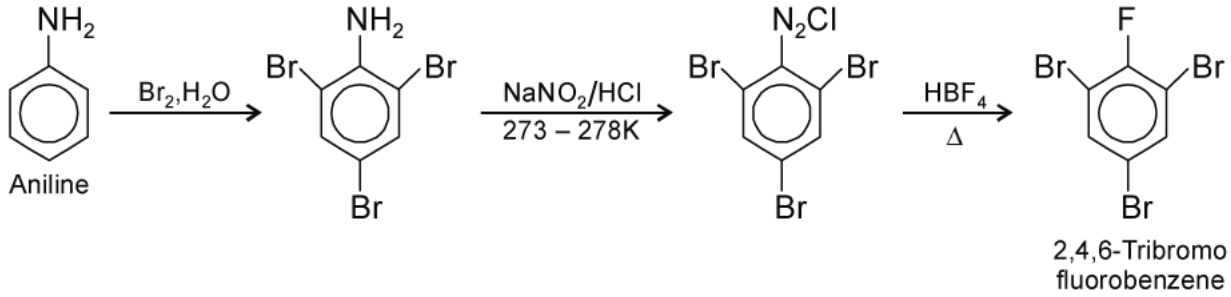

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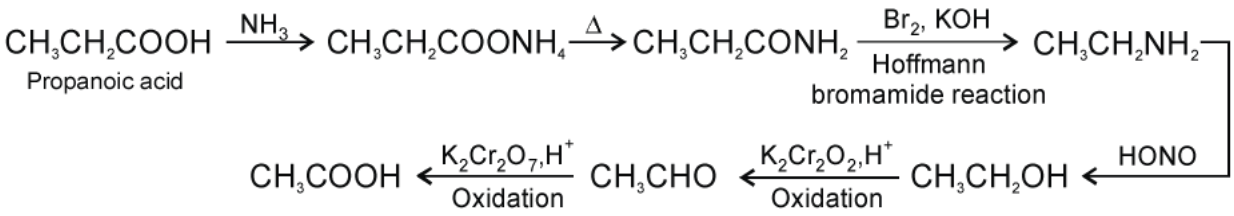

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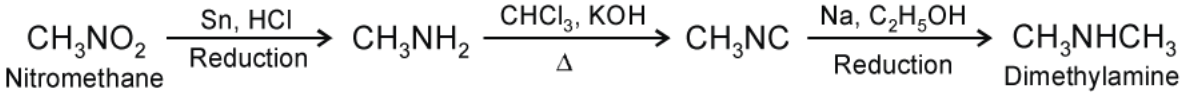

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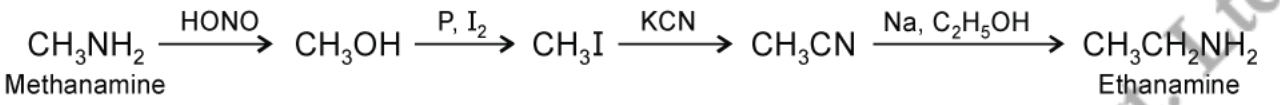

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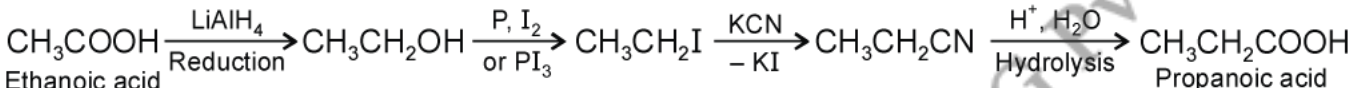

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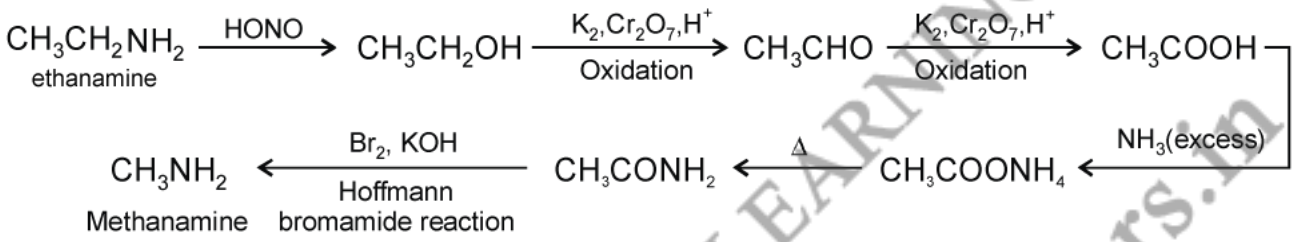

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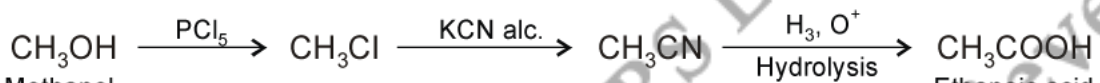

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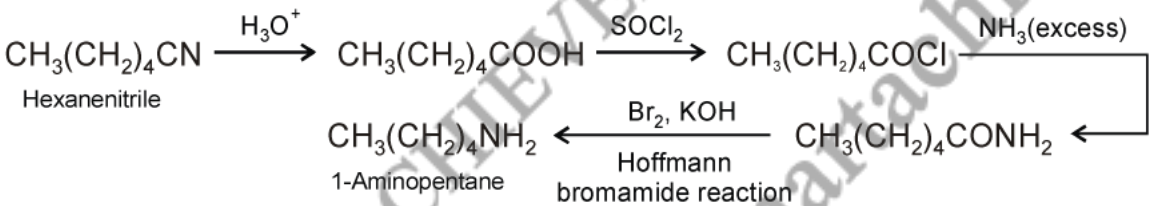

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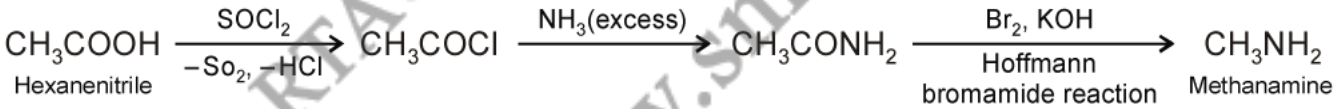

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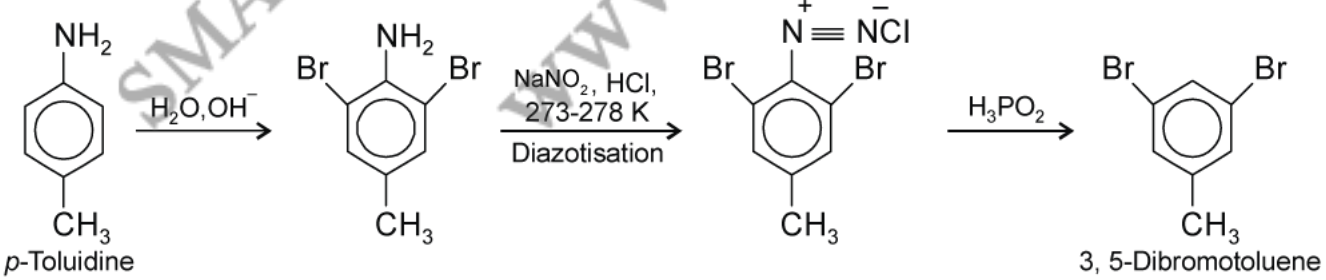

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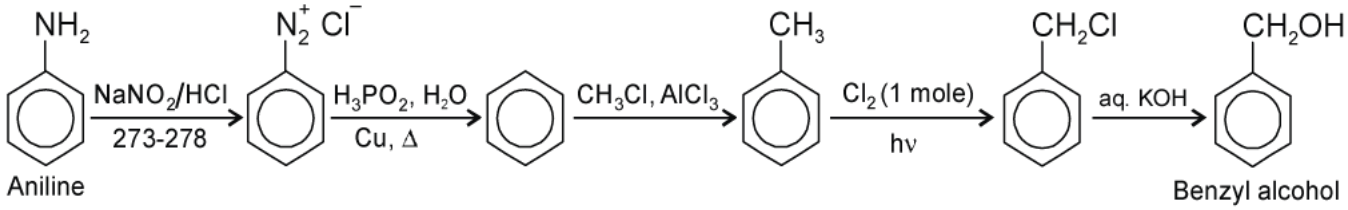

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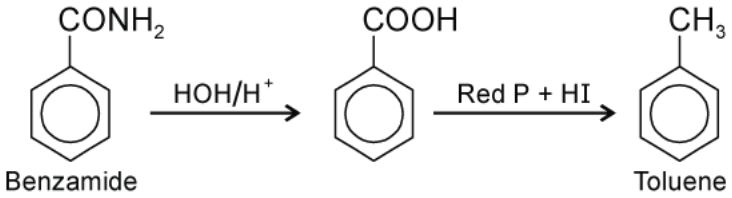

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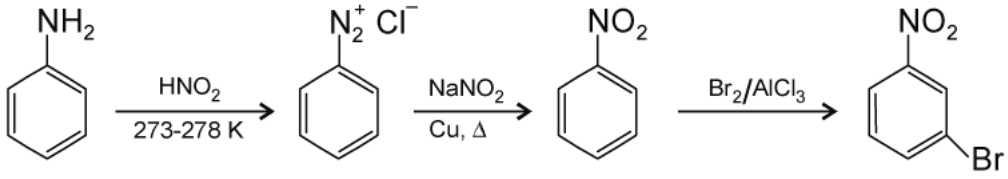
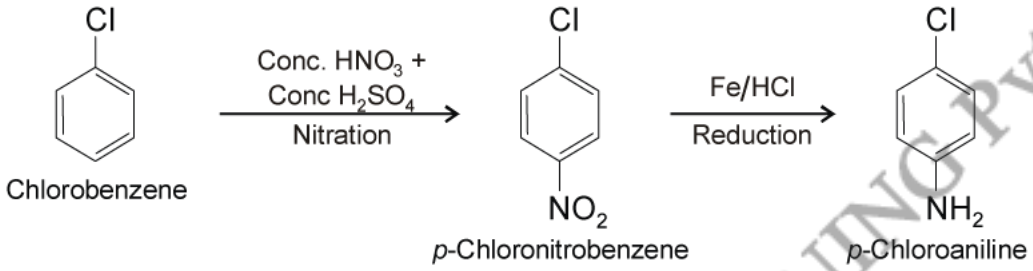
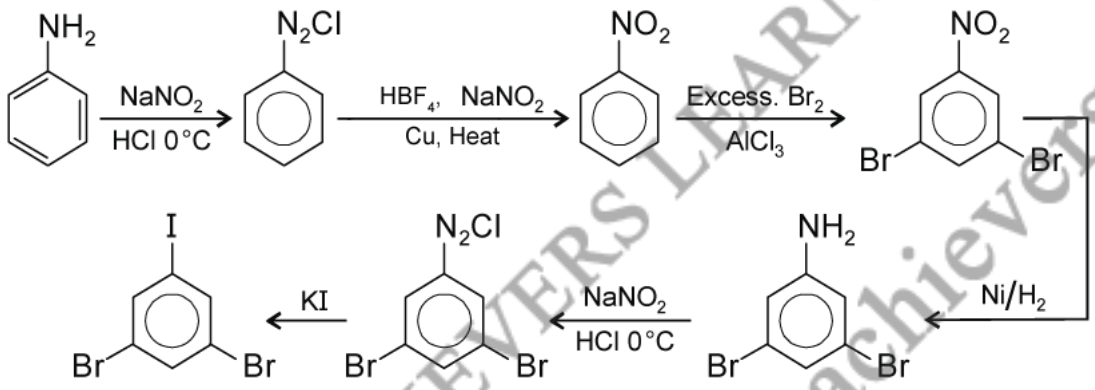


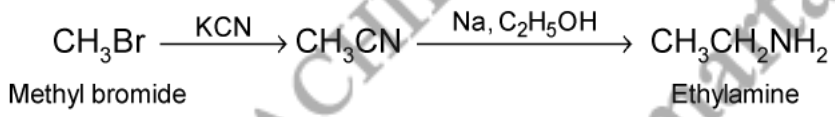
S26. Chlorobenzene to *p*-chloroaniline:



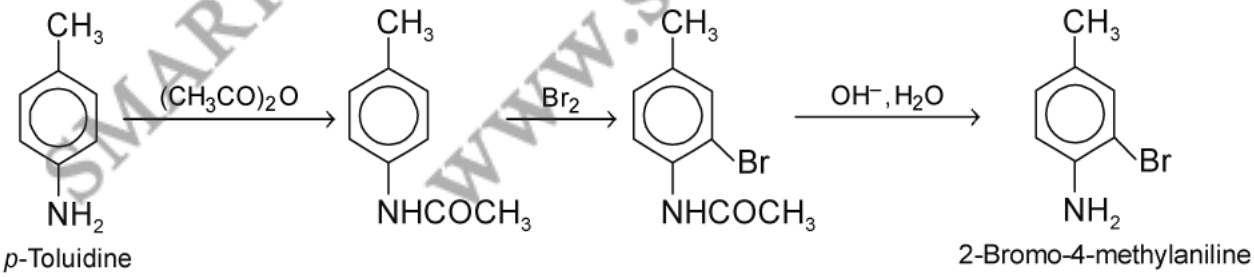
S27.



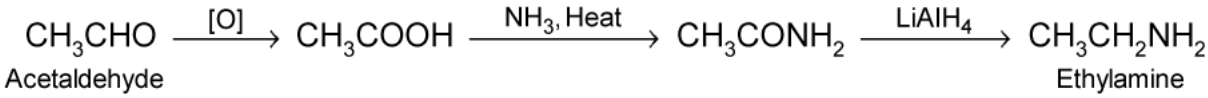
S28. (a)



(b)



(c)



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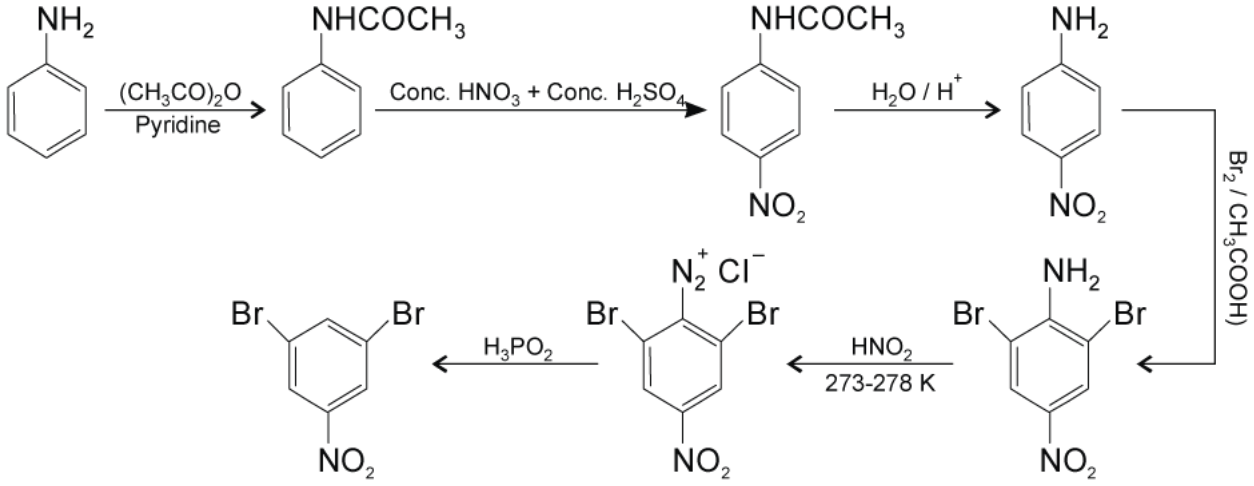

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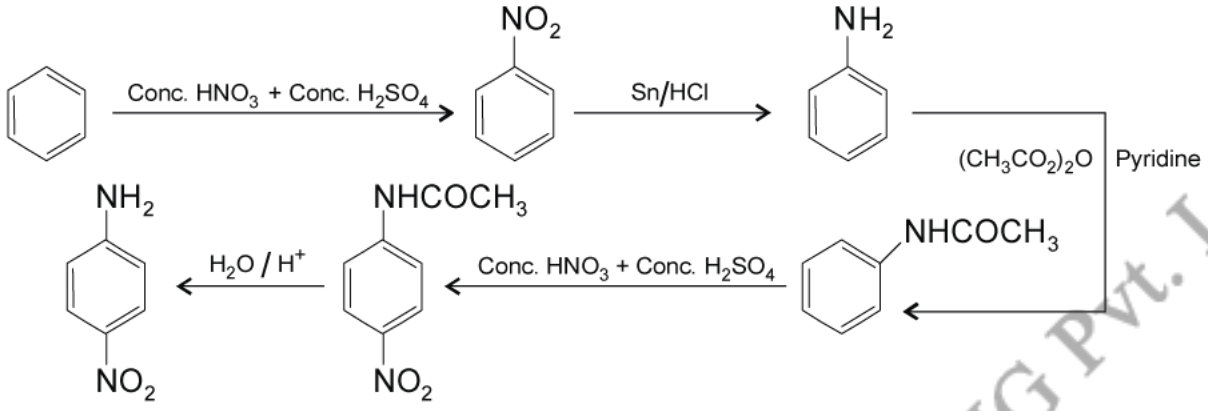
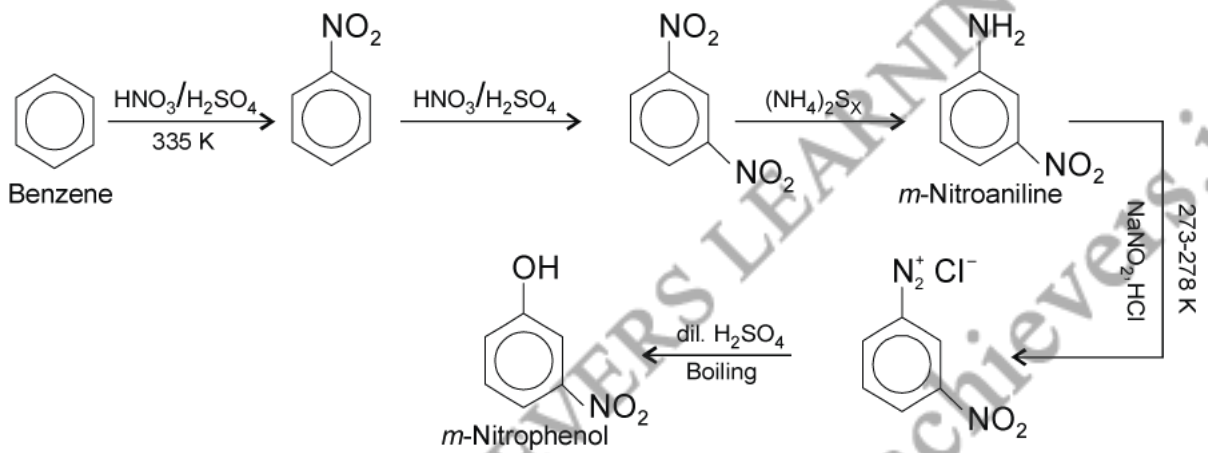
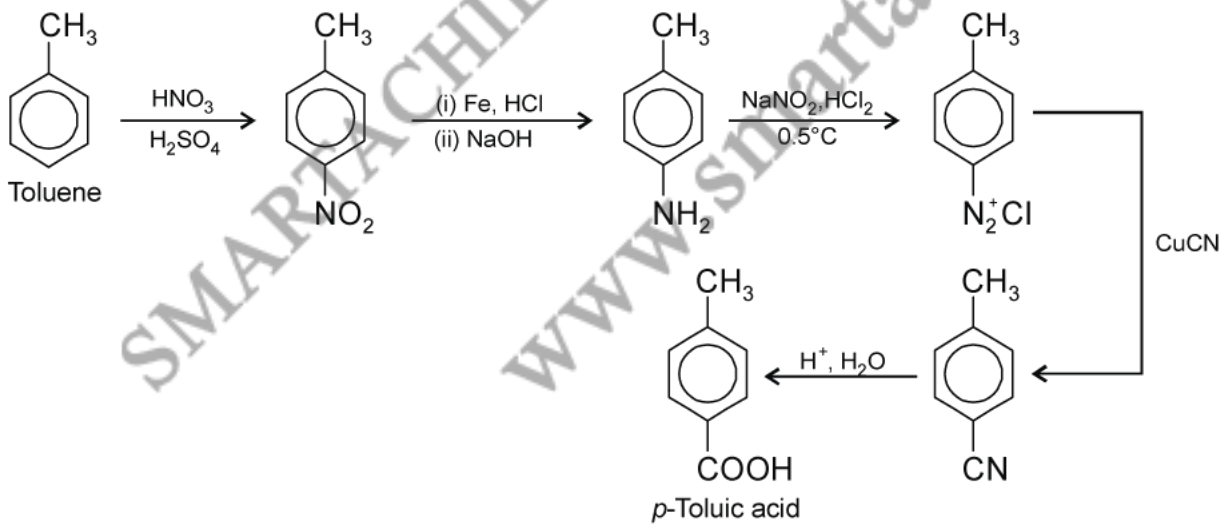


S31.



S32.



S33. (a) $C_6H_5CH_2NH_2 \xrightarrow[NaNO_2, HCl]{HONO} [C_6H_5CH_2NH_2]^+ Cl^- \xrightarrow[283\ K]{Water} C_6H_5CH_2OH$

Benzylamine — Benzyl alcohol

(b) $C_2H_5Cl \xrightarrow{NH_3} C_2H_5NH_2 \xrightarrow{C_2H_5Cl} C_2H_5-\underset{\underset{H}{|}}{N}-C_2H_5 \xrightarrow{C_2H_5Cl} C_2H_5-\underset{\underset{C_2H_5}{|}}{\overset{\overset{C_2H_5}{|}}{N}}$

N, N-Diethylethanamine

(c) $CH_3CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3CH_2CH_2Br \xrightarrow{KCN} CH_3CH_2CH_2CN \xrightarrow{LiAlH_4} CH_3CH_2CH_2CH_2NH_2$

Propene — Butylamine

Date: 26/10/2021

Q1. Give one chemical test to distinguish between methylamine and dimethylamine.

Q2. Describe the method for identification of primary, secondary and tertiary amines. Also write the chemical equations of the reactions involved.

Q3. Give one chemical test to distinguish between secondary and tertiary amines.

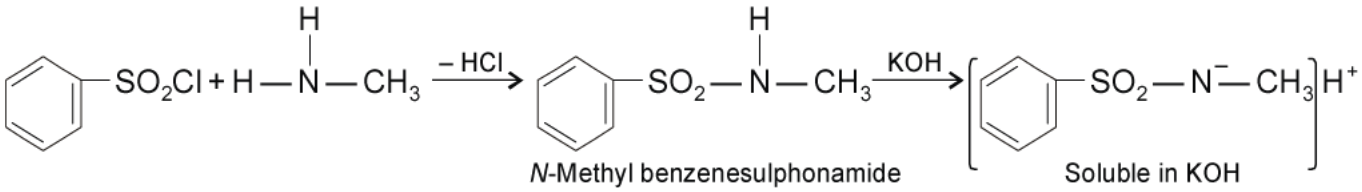
Q4. Give one chemical test to distinguish between ethylamine and aniline.

Q5. Give one chemical test to distinguish between aniline and benzylamine.

Q6. Give one chemical test to distinguish between aniline and *N*-methylaniline.

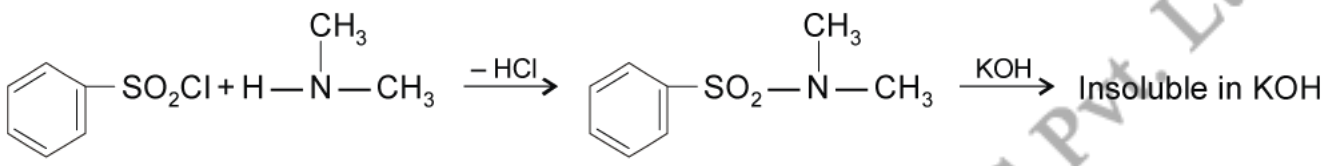
Date: 26/10/2021

S1. **Hinsberg Test: Methylamine (CH_3NH_2) (1°):** The product in case of methylamine is soluble in alkali and insoluble in acid.



N-Methyl benzenesulphonamide — Soluble in KOH

Hinsberg Test: Dimethylamine ($(CH_3)_2NH$ (2°): The product in case of dimethylamine is insoluble in alkali because it does not contain any hydrogen atom attached to nitrogen atom.



N, *N*-Methyl benzenesulphonamide

OR

Back up:

Carbylamine test methylamine:

$$CH_3NH_2 + CHCl_3 + 3KOH\ (alc.) \longrightarrow CH_3NC + 3KCl + 3H_2O$$

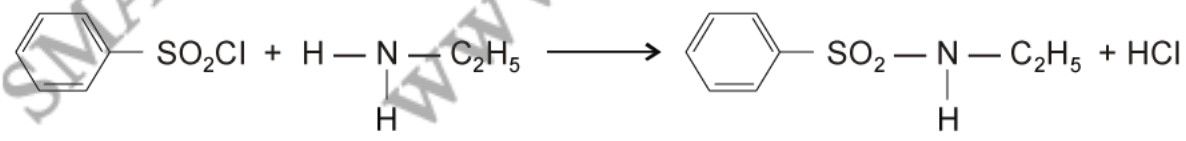
Methyl isocyanide (foul smell)

Carbylamine test of dimethylamine:

$$(CH_3)_2NH + CHCl_3 + 3KOH\ (alc.) \longrightarrow \text{No reaction}$$

S2. One method for the identification of primary, secondary and tertiary amines is ***Hinsberg's test***. Benzene sulphonyl chloride ($C_6H_5SO_2Cl$) which is also known as Hinsberg's regent, reacts with primary and secondary amines to form sulfonamides.

(a) The reaction of benzenesulphonyl chloride with primary amine yields *N*-ethyl-benzene-sulphonamide (I).

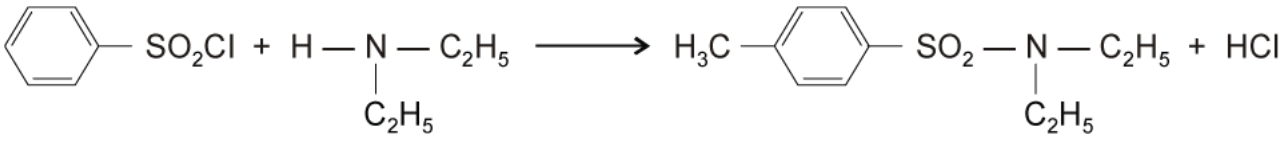


(I)

N-Ethylbenzenesulphonamide
(soluble in alkali)

The hydrogen attached to nitrogen in sulphonamide (I) is strongly acidic due to the presence of strongly electron withdrawing sulphonyl group. Hence, it is soluble in alkali.

(b) In the reaction with secondary amine, *N*, *N*-diethylbenzenesulphonamide (II) is formed.



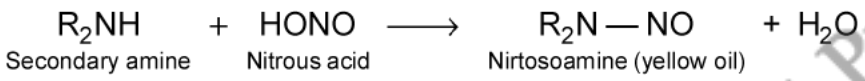
(II)

N, *N*-Diethylbenzenesulphonamide

Since structure II does not contain any hydrogen atom attached to nitrogen atom, it is not acidic and hence insoluble in alkali.

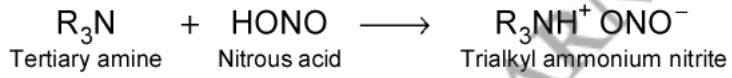
(c) Tertiary amines do not react with benzenesulphonyl chloride. This property of amines reacting with benzenesulphonyl chloride in different fashion is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. However, these days benzenesulphonyl chloride is replaced by *p*-toluenesulphonyl chloride.

S3. **Secondary amines with nitrous acid:** Secondary amines react with nitrous acid to form a yellow oily layer of *N*-nitrosoamines, which are insoluble in aqueous mineral acids.



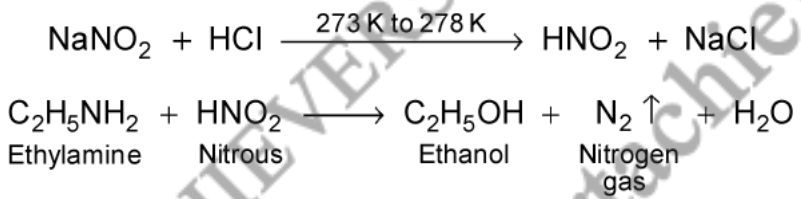
Secondary amine — Nitrous acid — Nirtosoamine (yellow oil)

Tertiary amines with nitrous acid: Tertiary aliphatic amines react with nitrous acid to form soluble nitrite salts with no visible change in reaction mixture.



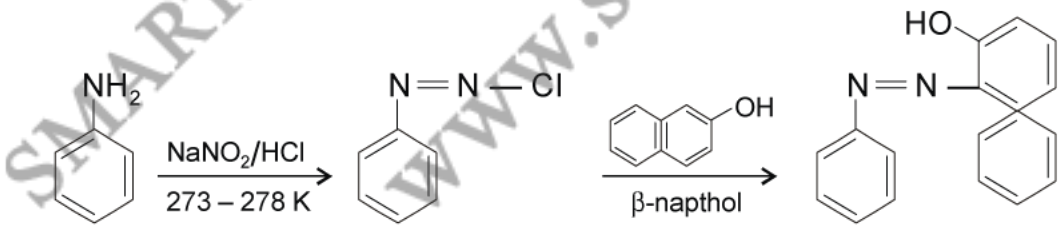
Tertiary amine — Nitrous acid — Trialkyl ammonium nitrite

S4. **Ethylamine ($C_2H_5NH_2$) with nitrous acid:** Ethylamine evolves nitrogen gas when reacted with nitrous acid.



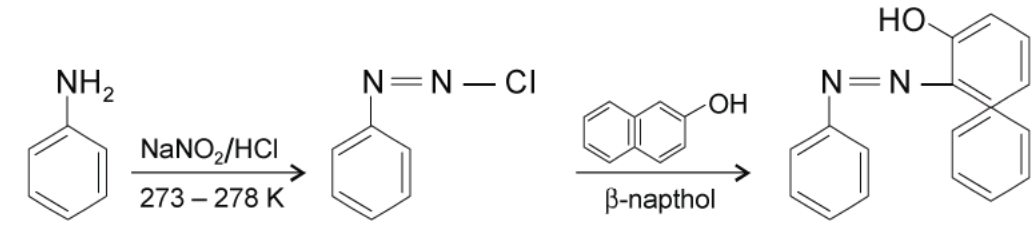
Ethylamine — Nitrous — Ethanol — Nitrogen gas

Aniline ($C_6H_5NH_2$) with nitrous acid: Aniline (all aromatic primary amines) diazotize in nitrous acid. The diazonium compound forms a briliant orange red dye with β-napthol in sodium hydroxide.

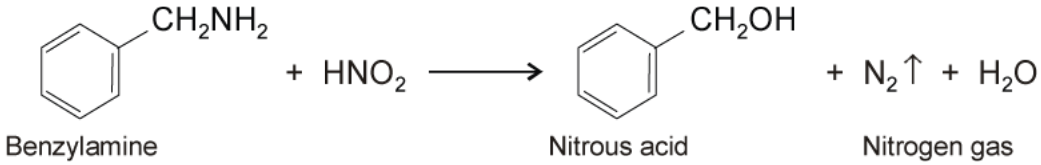


Aniline — Benzene diazonium chloride — (Orange red dye)

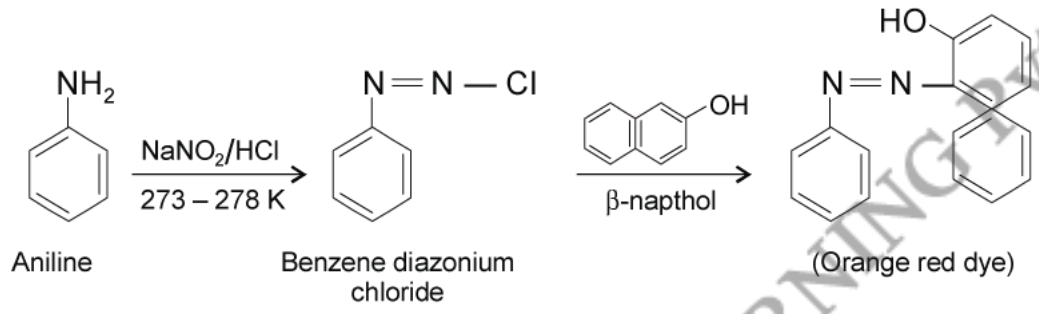
S5. **With nitrous acid: aniline ($C_6H_5NH_2$):** Aniline diazotize in nitrous acid. The diazonium compound froms a brilliant orange red dye with β-napthol in sodium hydroxide.



With nitrous acid: benzylamine ($C_6H_5CH_2NH_2$): Benzylamine will give nitrogen gas when react with nitrous acid.



S6. **Aniline ($C_6H_5NH_2$):** Aniline gives azodye test as described as below (all aromatic primary amines).



***N*-methylaniline ($C_6H_5NH.CH_3$):** Not give azodye test.