Term-II

AMINES

Syllabus

- ***Amines: Nomenclature, classification, structure, methods of preparation, physical and chemical properties, uses, identification of primary, secondary and tertiary amines.***

STAND ALONE MCQs

[1 Mark each]

Q. 1. CH_3CONH_2 on reaction with NaOH and Br_2 in alcoholic medium gives :

(A) $CH_3CH_2NH_2$ **(B)** CH_3CH_2Br

(C) CH_3NH_2 **(D)** CH_3COONa

U **[CBSE Delhi Set-I, 2020]**

Ans. Option (C) is correct.

Explanation:

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{Methylamine}}{CH_3NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

Q. 2. Propanamide on reaction with bromine in aqueous NaOH gives :

(A) Propanamine

(B) Ethanamine

(C) N-Methyl ethanamine

(D) Propanenitrile

OR

IUPAC name of product formed by reaction of methyl amine with two moles of ethyl chloride

(A) N,N-Dimethylethanamine

(B) N,N-Diethylmethanamine

(C) N-Methyl ethanamine

(D) N-Ethyl - N-methylethanamine

U **[CBSE SQP 2020-21]**

Ans. Option (B) is correct.

Explanation:

$$\underset{\text{Propanamide}}{CH_3CH_2CONH_2} + Br_2 + 4NaOH \xrightarrow{\Delta} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

This is Hoffman Bromamide reaction.

OR

Ans. Option (D) is correct.

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

Q. 3. Which of the following reagents would not be a good choice for reducing an aryl nitro compound to an amine ?

(A) H_2(excess)/Pt

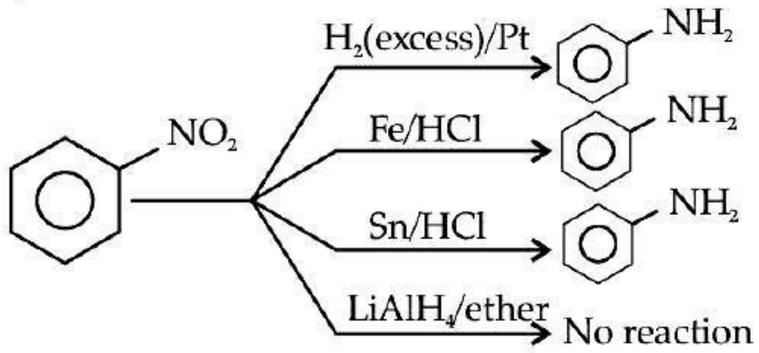
(B) $LiAlH_4$ in ether

(C) Fe and HCl

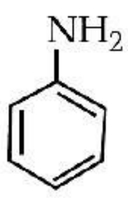
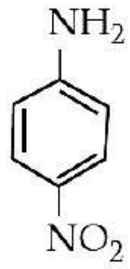
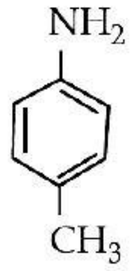
(D) Sn and HCl R

Ans. Option (B) is correct.

Explanation:



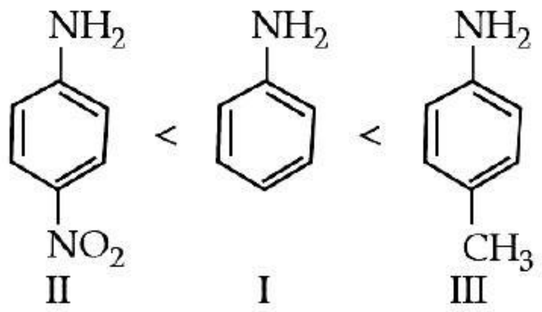
Q. 4. The correct increasing order of basic strength for the following compounds is _____.

(I)  (II)  (III) 

(A) II<III< I
(B) III < I < II
(C) III < II < I
(D) II < I < III A

Ans. Option (D) is correct.

Explanation:

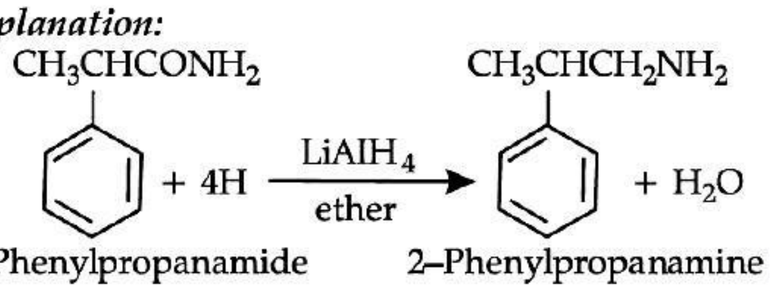


Electron withdrawing group decreases the basic strength while electron releasing groups increases the basic strength of aniline.

Q. 5. The best reagent for converting 2–phenylpropanamide into 2-phenylpropanamine is _____.
(A) excess H_2
(B) Br_2 in aqueous NaOH
(C) Iodine in the presence of red phosphorus
(D) $LiAlH_4$ in ether R

Ans. Option (D) is correct.

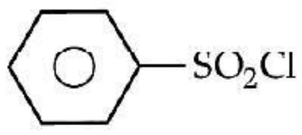
Explanation:



Q. 6. Hinsberg's reagent which is used to test amines is
(A) Benzene sulphonamide
(B) Benzene diazonium chloride
(C) Benzene sulphonyl chloride
(D) Acetanilide R

Ans. Option (C) is correct.

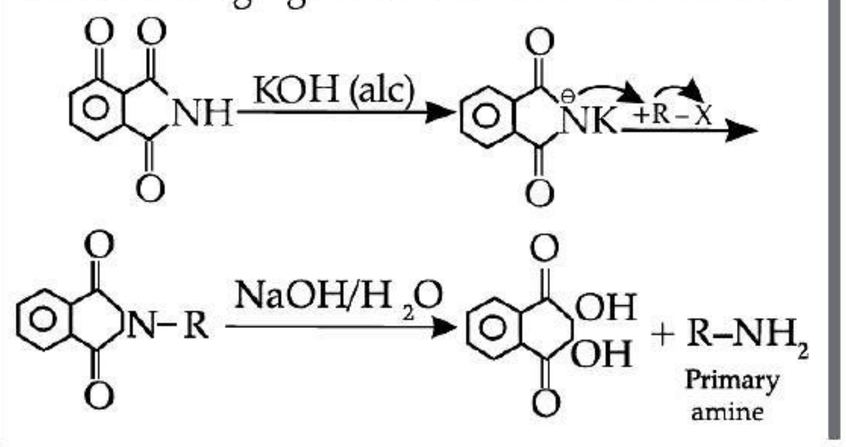
Explanation: Hinsberg's reagent which is used to test amines is benzene sulphonyl chloride.



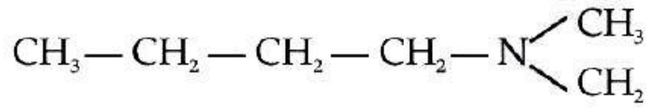
Q. 7. The best method for preparing primary amines from alkyl halides without changing the number of carbon atoms in the chain is :
(A) Hoffmann Bromamide reaction
(B) Gabriel phthalimide synthesis
(C) Sandmeyer reaction
(D) Reaction with NH_3 R

Ans. Option (B) is correct.

Explanation: Gabriel phthalimide synthesis is used to get primary amines from alkyl halides without changing the number of carbon atoms.



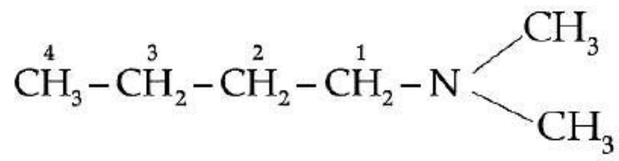
Q. 8. Write IUPAC name of the following compound :



(A) N,N-Dimethylpropanamine
(B) 1,1-Dimethylbutanamine
(C) N-Methylpentan-1-amine
(D) N,N-Dimethylbutan-1-amine U

Ans. Option (D) is correct.

Explanation:



IUPAC name: N, N – Dimethyl butan-1-amine

Q. 9. The correct IUPAC name for $CH_2 = CHCH_2NHCH_3$ is :
(A) Allylmethylamine
(B) 2-amino-4-pentene
(C) 4-aminopent-1-ene
(D) N-methylprop-2-en-1-amine U

Ans. Option (D) is correct.

Explanation: $C^3H_2 = C^2HC^1H_2\,NHCH_3$
IUPAC name: N-methylprop-2-en-1-amine

Q. 10. Which of the following is a 3° amine ?
(A) 1-methylcyclohexylamine
(B) Triethylamine
(C) *tert*-butylamine
(D) N-methylaniline R

Ans. Option (B) is correct.

Explanation: Triethylamine $[(C_2H_5)_3N]$ is a 3° or tertiary amine as nitrogen atom contains three ethyl groups.

Q. 11. Methylamine reacts with HNO_2 to form _____.
(A) $CH_3 — O — N = O$
(B) $CH_3 — O — CH_3$
(C) CH_3OH
(D) CH_3CHO

OR

The gas evolved when methylamine reacts with nitrous acid is :
(A) NH_3 **(B)** N_2
(C) H_2 **(D)** C_2H_6

Ans. Option (C) is correct.

Explanation: Methylamine reacts with HNO_2 to form CH_3OH.

$$\underset{\text{methyl amine}}{CH_3NH_2} + HNO_2 \xrightarrow{NaNO_2+HCl} CH_3 - N_2^+Cl^- \xrightarrow{H_2O} CH_3OH + N_2 + HCl$$

OR

Ans. Option (B) is correct.

Explanation: Nitrogen gas is evolved.

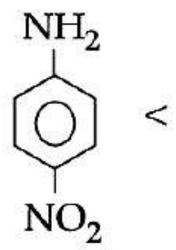
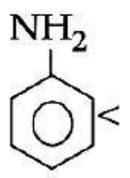
Q. 12. Arrange the following in increasing order of basic strength :

Aniline, p-nitroaniline and p-toludine.

(A) Aniline < p-Nitroaniline < p-Toluidine
(B) Aniline < p-Toluidine < p-Nitroaniline
(C) p-Toluidine < p-Nitroaniline < Aniline
(D) p-Nitroaniline < Aniline < p-Toluidine AE

Ans. Option (D) is correct.

Explanation: The increasing order of basic strength is given as below :

 p-Nitroanline	 Aniline	 p-Toluidine
I effect of NO_2 group decreases the electron density on N-atom of $-NH_2$ group, so, it does not undergo protonation easily and hence, it is least basic amine.	It does not contain –I or +I group.	+I effect of CH_3 group increases the electron density on the nitrogen atom of $-NH_2$ group, so, it undergo protonation easily and hence, it is most basic amine.

Q. 13. Which of the following species are involved in the carbylamine test ?

(A) R—NC **(B)** $COCl_2$
(C) $NaNO_2$ + HCl **(D)** All of the above

Ans. Option (A) is correct.

Explanation: In the carbylamine test, a primary amine reacts with chloroform and KOH to form alkyl isocyanide (i.e. R–NC) having unpleasant smell.

Q. 14. Which of the following amines can be prepared by Gabriel synthesis ?

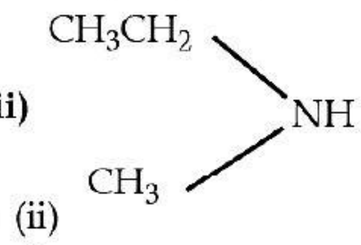
(A) Isobutyl amine
(B) Toluene
(C) N-methylbenzylamine
(D) Aniline U

Ans. Option (A) is correct.

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

Q. 15. Which of the following should be most volatile ?

(i) $CH_3CH_2NH_2$ **(ii)** $(CH_3)_3N$

(iii) 

(iv) $CH_3CH_2CH_3$

(A) (ii) **(B)** (iv)
(C) (i) **(D)** (iii) A

Ans. Option (B) is correct.

Explanation: Primary and secondary amines form hydrogen bonds and hence are less volatile than corresponding alkanes.

ASSERTION AND REASON BASED MCQs [1 Mark each]

Directions: In the following questions, A statement of Assertion (A) is followed by a statement of Reason (R). Mark the correct choice as.

(A) Both A and R are true and R is the correct explanation of A
(B) Both A and R are true but R is NOT the correct explanation of A
(C) A is true but R is false
(D) A is false and R is True

Q. 1. Assertion (A): Acylation of amines gives a monosubstituted product whereas alkylation of amines gives poly substituted product.

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

Ans. Option (C) is correct.

Explanation: In alkylation, an amine can react with alkyl halide to form next higher class of amine caused by the presence of electron pair on nitrogen which makes amine to behave as nucleophile and alkyl halide thus undergo nucleophilic substitution reaction. When primary and secondary amines react with acid chlorides, anhydrides and esters to give monosubstituted amides as products. Acylation is carried out in the presence of a base stronger than the amine like pyridine which causes the shift of the equilibrium to the right side.

Q. 2. Assertion (A): Acetanilide is less basic than aniline.

Reason (R): Acetylation of aniline results in decrease of electron density on nitrogen.

Ans. Option (A) is correct.

Explanation: Acetanilide is less basic than aniline as in amides the carbonyl group (C=O) is a stronger dipole than N-C dipole. Therefore, the ability of N-C group to act as H-bond acceptor (as a base) is restricted in the presence of a C=O dipole.

Q. 3. Assertion (A): N, N-Diethylbenzene sulphonamide is insoluble in alkali.

Reason (R): Sulphonyl group attached to nitrogen atom is strong electron withdrawing group.

Ans. Option (A) is correct.

Explanation: N,N-Diethylbenzenesulphonamide is insoluble in alkali because it has no acidic hydrogen. Sulphonyl group attached to nitrogen atom is electron withdrawing group.

Q. 4. Assertion (A): Aromatic 1° amines can be prepared by Gabriel Phthalimide synthesis.

Reason (R): Aryl halides do not undergo nucleophilic substitution with anion formed by phthalimide.

Ans. Option (D) is correct.

Explanation: Aromatic 1° amines cannot be prepared by Gabriel Phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with anion formed by phthalimide.

CASE-BASED MCQs

I. Read the passage given below and answer the following questions:

Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order. Secondly, when the alkyl group is small, like $-CH_3$ group, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than CH_3 group, there will be steric hinderance to H-bonding. Therefore, the change of nature of the alkyl group, e.g., from $-CH_3$ to $-C_2H_5$ results in change of the order of basic strength.

In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(A) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(B) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(C) Assertion is correct statement but reason is wrong statement.

(D) Assertion is wrong statement but reason is correct statement.

Q. 1. Assertion (A): $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ is the order of basic strength in case of methyl substituted amines.

Reason (R): The inductive effect, solvation effect and steric hindrance of the alkyl group decides the basic strength of alkyl amines in the aqueous state.

Ans. Option (A) is correct.

Explanation: $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ is the order of basic strength in case of methyl substituted amines as the inductive effect, solvation effect and steric hinderance of the alkyl group decides the basic strength of alkyl amines in the aqueous state.

Q. 2. Assertion (A): $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ is the order of basic strength in case of ethyl substituted amines.

Reason (R): The change of nature of the alkyl group, does not result in change of the order of basic strength.

Ans. Option (C) is correct.

Explanation: $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ is the order of basic strength in case of ethyl substituted amines. The change of nature of the alkyl group, results in change of the order of basic strength.

Q. 3. Assertion (A): Greater is the stability of the substituted ammonium cation, stronger is the corresponding amine as a base.

Reason (R): The order of basicity of aliphatic amines is: primary > secondary > tertiary.

Ans. Option (C) is correct.

Explanation: Greater is the stability of the substituted ammonium cation, stronger is the corresponding amine as a base but the inductive effect, solvation effect and steric hinderance of the alkyl group decides the basic strength of alkyl amines in the aqueous state.

Q. 4. Assertion (A): Amines behave as a Lewis base.

Reason (R): Amines have an unshared pair of electrons on nitrogen atom.

OR

Ans. Option (A) is correct.

Explanation: Amines behave as a Lewis base as they have an unshared pair of electrons on nitrogen atom.

Assertion (A): Solubility of amines in water decreases with increase in molar mass.

Reason (R): Intermolecular H bonds formed by the higher amines are weaker.

Ans. Option (C) is correct.

Explanation: Lower aliphatic amines are soluble in water because they can form hydrogen bonds with water molecules. However, solubility decreases with increase in molar mass of amines due to increase in size of the hydrophobic alkyl part.

II. Read the passage given below and answer the following questions : **(1 × 4 = 4)**

Benzene ring in aniline is highly activated. This is due to the sharing of lone pair of nitrogen with the ring which results in increase in the electron density on the ring and hence facilitates the electrophilic attack. The substitution mainly takes place at ortho and para positions because electron density is more at ortho and para positions. On reaction with aqueous bromine all the ortho and para positions get substituted resulting in the formation of 2,4,6-tribromoaniline. To get a monobromo compound, the amino group is acetylated before bromination. After bromination, the bromoacetanilide is acid hydrolysed to give the desired halogenated amine.

In the following questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices :

(A) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(B) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(C) Assertion is correct statement but reason is wrong statement.

(D) Assertion is wrong statement but reason is correct statement.

Q. 1. Assertion (A): Benzene ring is aniline is highly deactivated.

Reason (R): In aniline, the sharing of lone pair of nitrogen with the ring increases the electron density on the ring.

Ans. Option (D) is correct.

Explanation: Benzene ring in aniline is highly activated.

Q. 2. Assertion (A): In aniline $-NH_2$ group facilitates the electrophilic attack.

Reason (R): It is due to decrease in electron density on the ring.

Ans. Option (C) is correct.

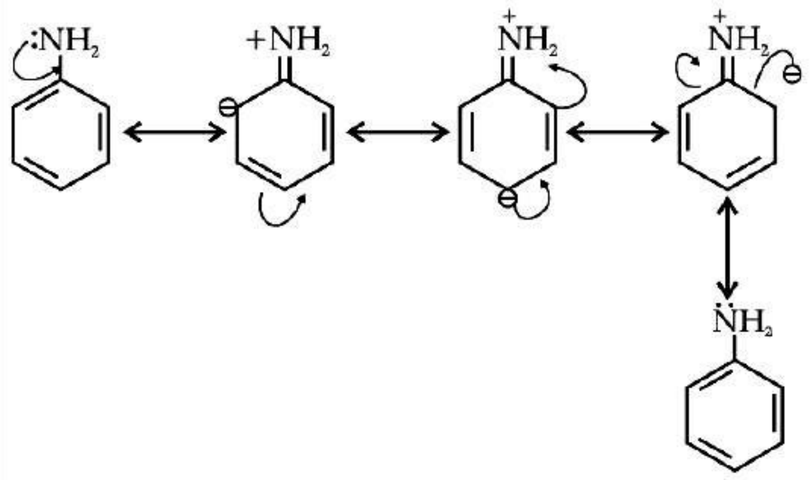
Explanation: In aniline, $-NH_2$ group facilitates the electrophilic attack because the sharing of lone pair of nitrogen with the ring increases the electron density on the ring.

Q. 3. Assertion (A): In aniline, the substitution mainly takes place at ortho and para positions.

Reason (R): The electron density is more at ortho and para positions.

Ans. Option (C) is correct.

Explanation: In aniline, the electron density is more at ortho and para positions than meta position, so, the substitution mainly takes place at ortho and para positions.



The above resonating structures of aniline show more electron density at the ortho and para positions.

Q. 4. Assertion (A): The amino group of aniline is acetylated before bromination.

Reason (R): It is due to the strong deactivating effect of $-NH_2$ group.

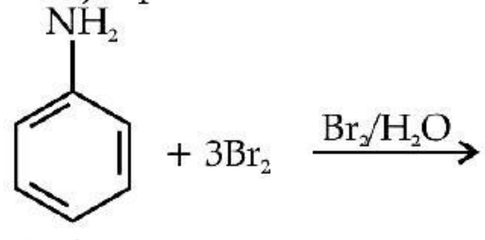
Ans. Option (C) is correct.

Explanation: $-NH_2$ group of aniline is acetylated before bromination due to the strong activating effect of $-NH_2$ group.

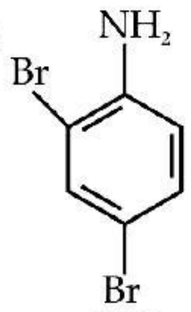
III. Read the passage given below and answer the following questions :

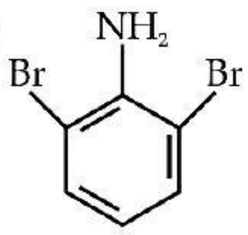
The main problem encountered during electrophilic substitution reactions of aromatic amines is that of their very high reactivity. Substitution tends to occur at ortho and para-positions. If we have to prepare monosubstituted aniline derivative, how can the activating affect of $-NH_2$ group be controlled? This can be done by protecting the $-NH_2$ group by acetylation with acetic anhydride, then carrying out the desired substitution followed by hydrolysis of the substituted amide to the substituted amine.

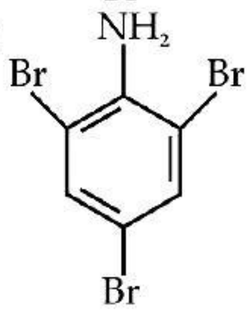
Q. 1. Give the major product of the following reaction:



Aniline

(A) 

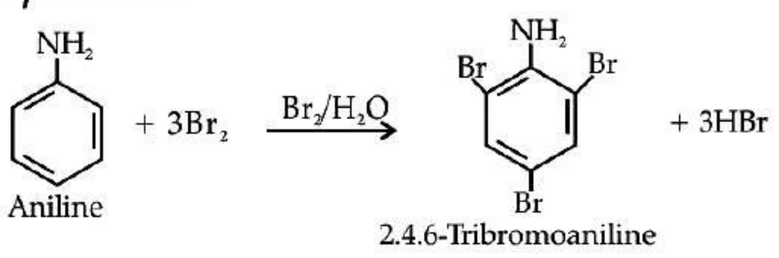
(B) 

(C) 

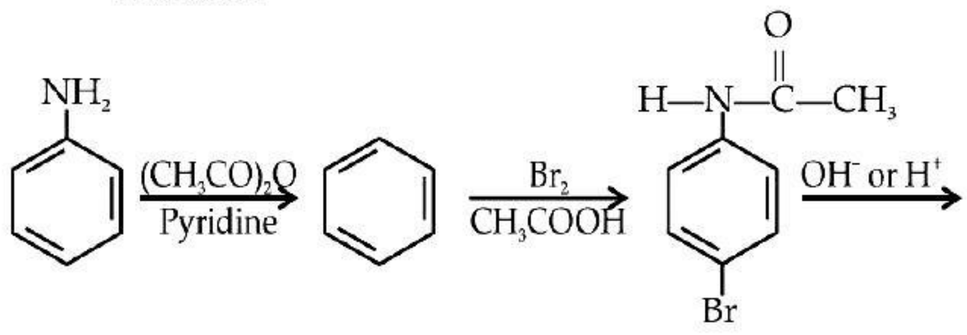
(D) None of the above

Ans. Option (C) is correct.

Explanation:



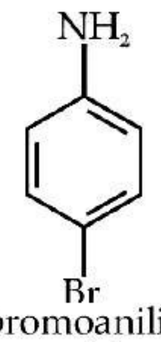
Q. 2. What is the major product A of the following reaction:



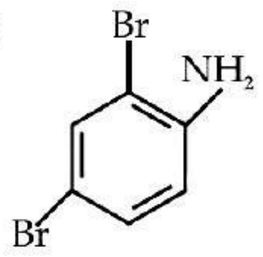
Aniline N-Phenylethanamide (Acetanilide) (Major)

(A) 

2-bromoaniline

(B) 

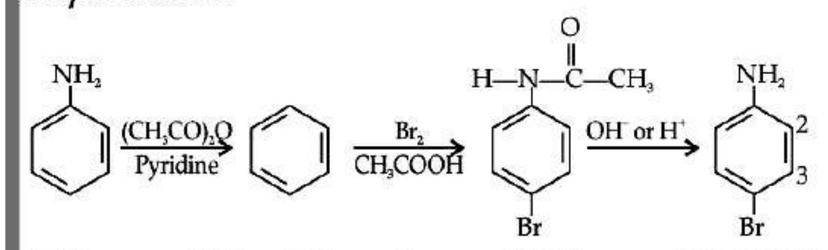
4-bromoaniline

(C) 

(D) None of the above

Ans. Option (B) is correct.

Explanation:



Q. 3. Why is the activating effect of -$NHCOCH_3$ group in the above reaction less than the activating effect of amino group?

(A) Due to mesomeric effect of benzene ring.

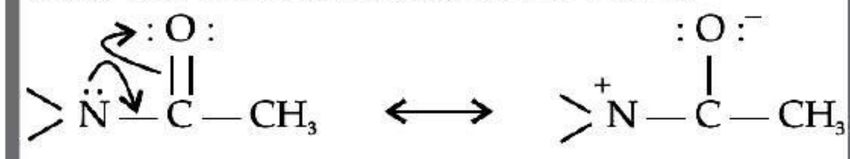
(B) Due to inductive effect of alkyl group.

(C) Due to resonance effect of acetanilide.

(D) All of the above.

Ans. Option (C) is correct.

Explanation: 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 benzene ring by resonance. Therefore, activating effect of –$NHCOCH_3$ group is less than that of amino group.

Q. 4. Aniline is a resonance hybrid of

(A) 3 structures (B) 6 structures

(C) 2 structures (D) 5 structures

Ans. Option (D) is correct.

Explanation: Aniline is a resonance hybrid of 5 structures.