# Amines JEE Main PYQ - 1

**Total Time:** 1 Hour : 15 Minute **Total Marks:** 120

## Instructions

## Instructions

1. Test will auto submit when the Time is up.
2. The Test comprises of multiple choice questions (MCQ) with one or more correct answers.
3. The clock in the top right corner will display the remaining time available for you to complete the examination.

### Navigating & Answering a Question

1. The answer will be saved automatically upon clicking on an option amongst the given choices of answer.
2. To deselect your chosen answer, click on the clear response button.
3. The marking scheme will be displayed for each question on the top right corner of the test window.

# Amines

1. **Which of the following reaction is correctly matched with their product ?** **(+4, -1)**

   **a.** Phthalimide reaction forming Aniline

   **b.** $CH_3CH_2CONH_2 + Br_2 + 4KOH \rightarrow CH_3CH_2NH_2$

   **c.** Carbylamine reaction forming nitrile

   **d.** Reduction of amide with $LiAlH_4$ forming nitrile

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2. **Statement-I :** $KMnO_4 \xrightarrow{\Delta} NH_2$ **followed by** $Br_2/KOH \rightarrow NH_2$. **(+4, -1)**
   **Statement-II :** $CH_3NH_2 \xrightarrow{(i)\ Br_2/H_2O,(ii)\ NaNO_2/HCl,(iii)\ H_3PO_2/\Delta} CH_3Br$.

   **a.** Statement-I and Statement-II both are correct

   **b.** Statement-I is incorrect Statement-II is correct

   **c.** Statement-I is correct Statement-II is incorrect

   **d.** Statement-I and Statement-II both incorrect

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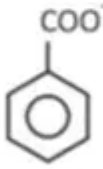
3. **Observe the following reaction sequence:** **(+4, -1)**
   \text{(P) }\xrightarrow{\text{NH}_3, \Delta} \text{(Q)}
   \xrightarrow{\text{Br}_2, \text{KOH}} \text{(R)}
   **Which of the following is the correct structure for P, Q, and R?**

(1) P =  , Q =  , R = 

(2) P =  , Q =  , R = 

(3) P =  , Q =  , R = 

(4) P =  , Q =  , R = 

a. 1

b. 2

c. 3

d. 4

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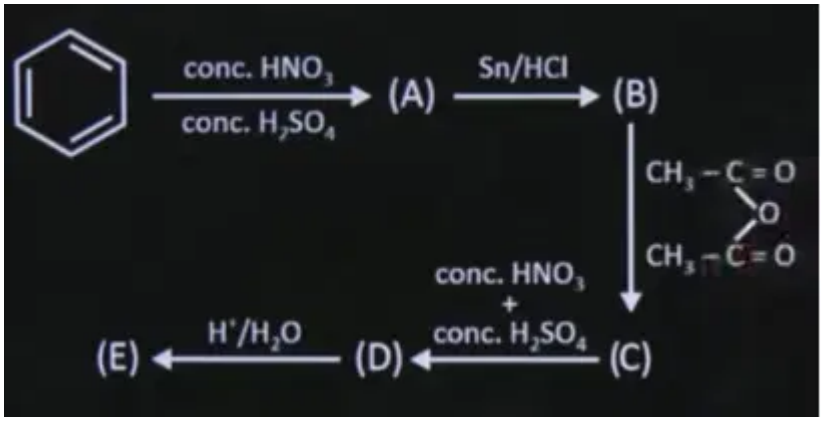
4. Benzene undergoes the following sequence of reactions: (+4, -1)




Find the percentage of nitrogen in compound $(E)$.

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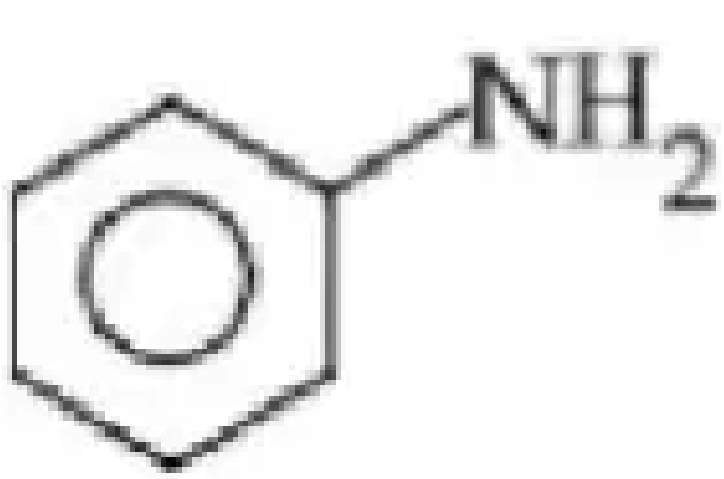
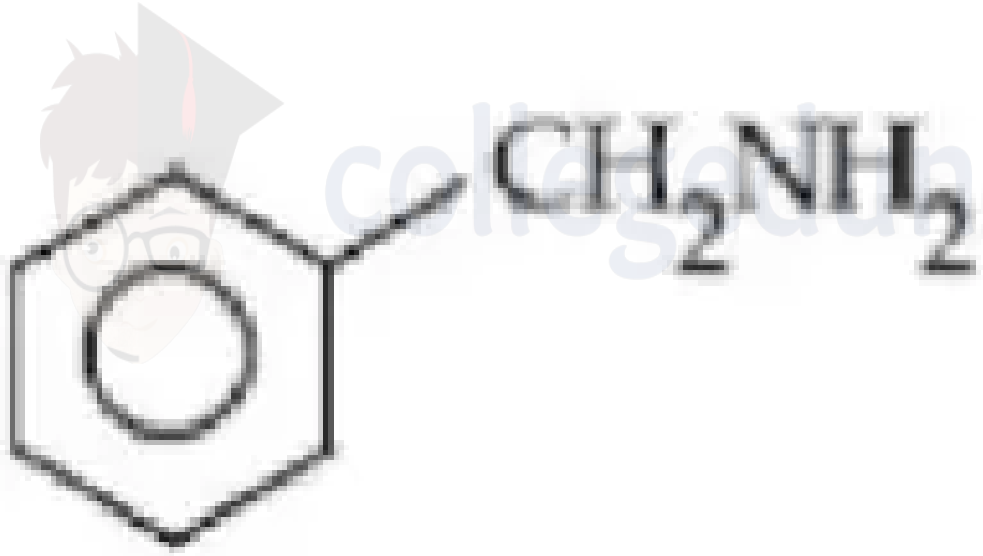
5. 1.86 g of aniline completely reacts to form acetanilide. 10% of the product is lost during purification. Amount of acetanilide obtained after purification (in g) is (+4, -1)

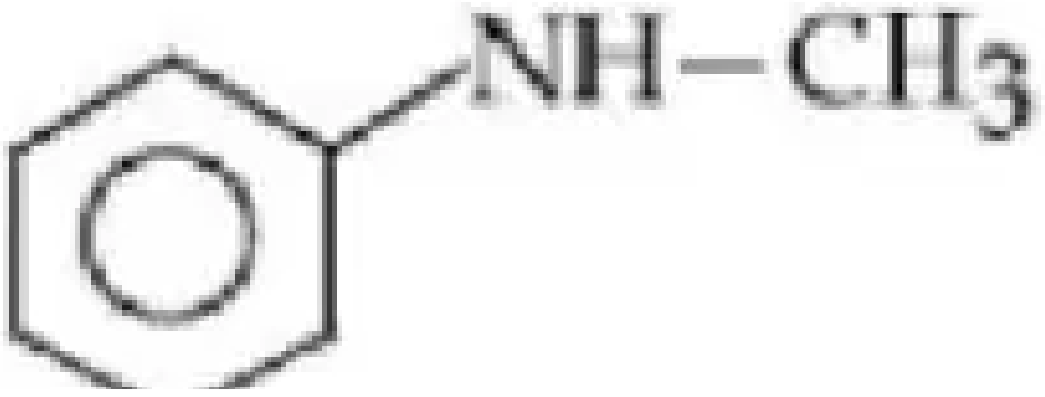
_____ × $10^{-2}$.

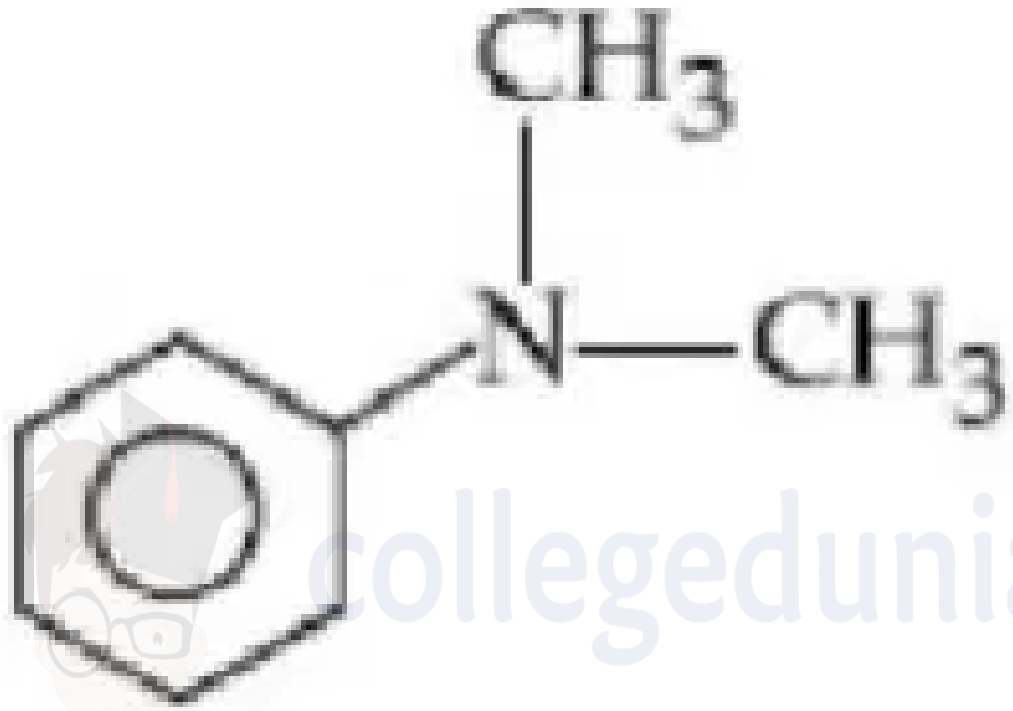
6. The total number of amines among the following which can be synthesized by Gabriel synthesis is _____. (A) ethylamine, (B) n-propylamine, (C) benzylamine, (D) aniline (+4, -1)

7. The diazonium salt of which of the following compounds will form a coloured dye on reaction with β-Naphthol in NaOH ? (+4, -1)


NH2


CH2NH2


NH—CH3



a. A

b. B

c. C

d. D

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8. A reaction of 0.1 mole of Benzylamine with bromomethane gave 23 g of Benzyl trimethyl ammonium bromide. The number of moles of bromomethane consumed in this reaction are n × $10^{-1}$, when n = _____. (Round off to the Nearest Integer). (+4, -1)

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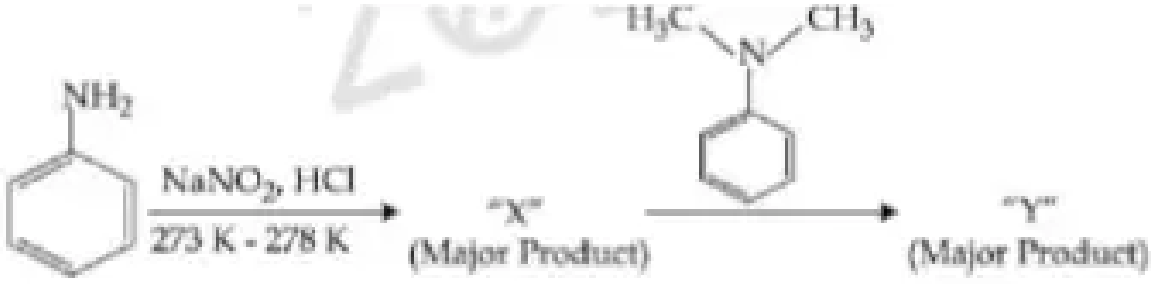
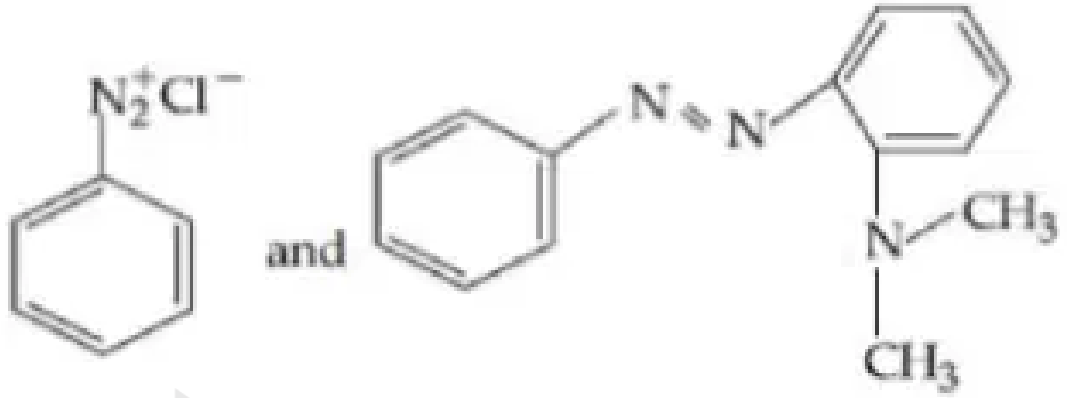
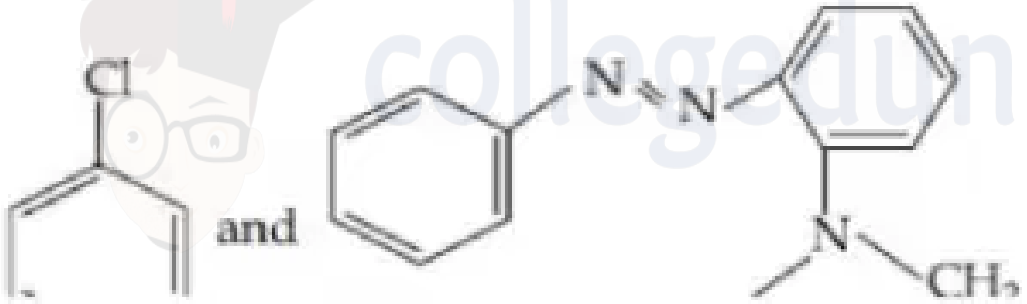
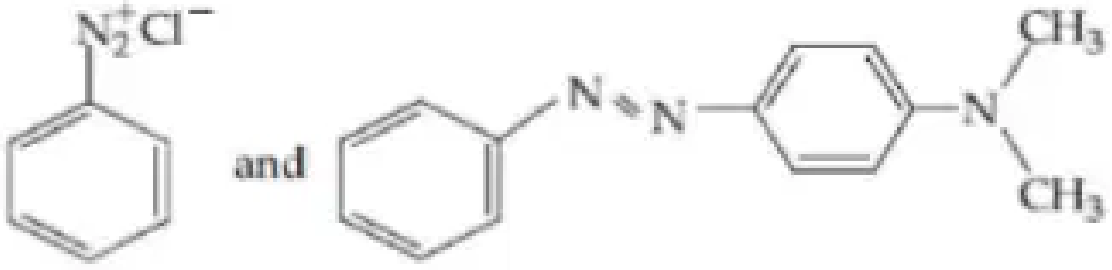
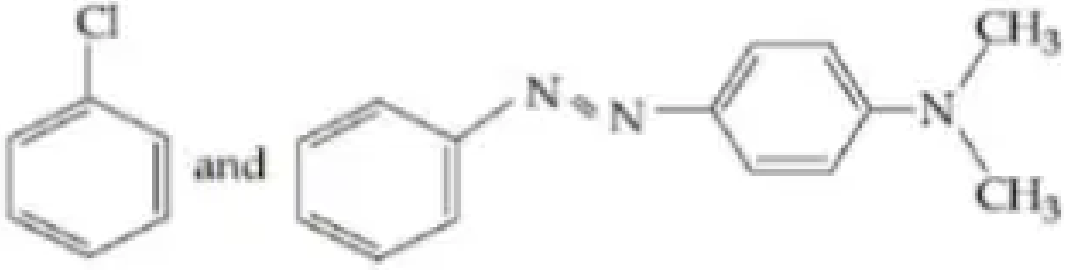
9. Considering the reaction of Aniline with $NaNO_2/HCl$ at $0-5^{\circ}$C to give X, which is then reacted with $H_3PO_2$, identify X and Y : (+4, -1)


NH2
NaNO2, HCl
273 K - 278 K
"X"
(Major Product)
H3C
N
CH3
"Y"
(Major Product)


N2+Cl−
and
N
N
N
CH3
CH3


Cl
and
N
N
N
CH3


N2+Cl−
and
N
N
N
CH3
CH3


Cl
and
N
N
N
CH3
CH3

a. A

b. B

c. C

d. D

---

10. Given below are two statements, one is labelled as Assertion (A) and other is labelled as Reason (R). (+4, -1)
Assertion (A) : Gabriel phthalimide synthesis cannot be used to prepare aromatic primary amines.
Reason (R) : Aryl halides do not undergo nucleophilic substitution reaction.
In the light of the above statements, choose the correct answer from the options given below :

a. Both (A) and (R) are true and (R) is 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 but (R) is true.

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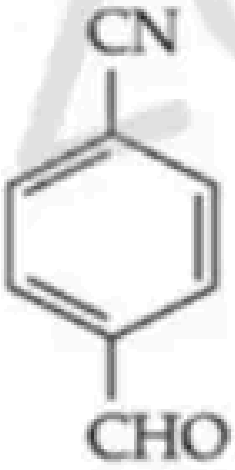
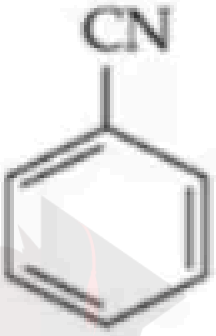
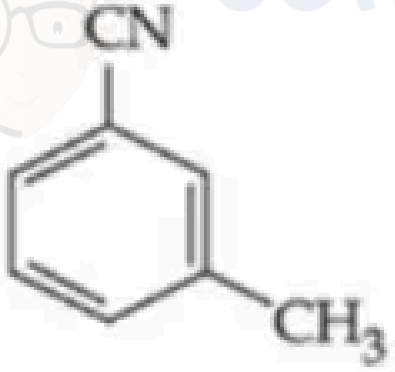
11. Which one of the products of the following reactions does not react with Hinsberg reagent to form sulphonamide? (+4, -1)

(A) 

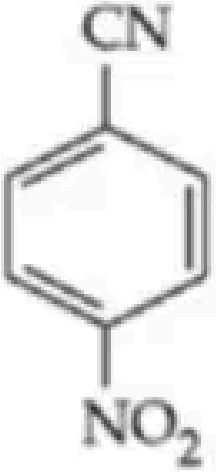
$+ LiAlH_4 \xrightarrow{H_3O^{\oplus}}$

(B) 

$+ SnCl_2 + HCl \longrightarrow$

(C) 

$+ H_2/Ni \longrightarrow$

(D) 

$+ Na/Hg \xrightarrow{C_2H_5OH}$

a. A

b. B

c. C

d. D

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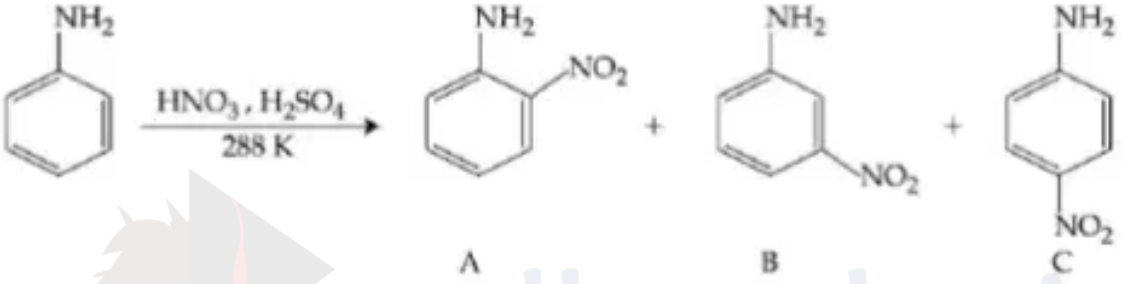
12. Consider the given reaction, percentage yield of : (+4, -1)




a. $A > C > B$

b. $C > A > B$

c. $B > C > A$

d. $C > B > A$

---

13. An organic compound "A" on treatment with benzene sulphonyl chloride gives compound B. B is soluble in dil. NaOH solution. Compound A is : (+4, -1)

a. $C_6H_5 - CH_2 - NH - CH_3$

b. $C_6H_5 - N(CH_3)_2$

c. $C_6H_5 - NH - CH_2 - CH_3$

d. $C_6H_5 - CH_2 - NH_2$

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14. In the reaction of hypobromite with amide, the carbonyl carbon is lost as : (+4, -1)

a. CO

b. $CO_2$

c. $CO_3^{2-}$

d. $HCO_3^-$

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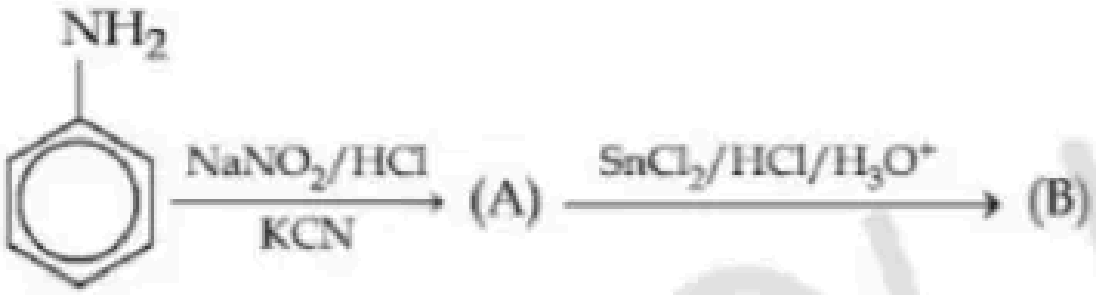
15. 'A' and 'B' in the following reactions ($C_6H_5NH_2 \xrightarrow{CHCl_3/KOH} A \xrightarrow{H_2O/H^+} B$) are : (+4, -1)


NH2
NaNO2/HCl
KCN
(A)
SnCl2/HCl/H3O+
(B)


(A) :
N2Cl
(B) :
Cl

.

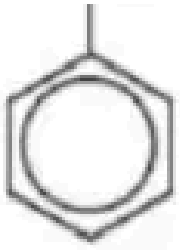

(A) :
N2Cl
(B) :
CHO

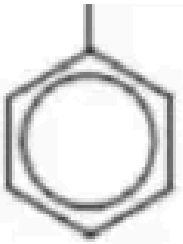
.


(A) :
CN
(B) :
Cl

.


CN
CHO

(A) : 

(B) : 

a. A

b. B

c. C

d. D

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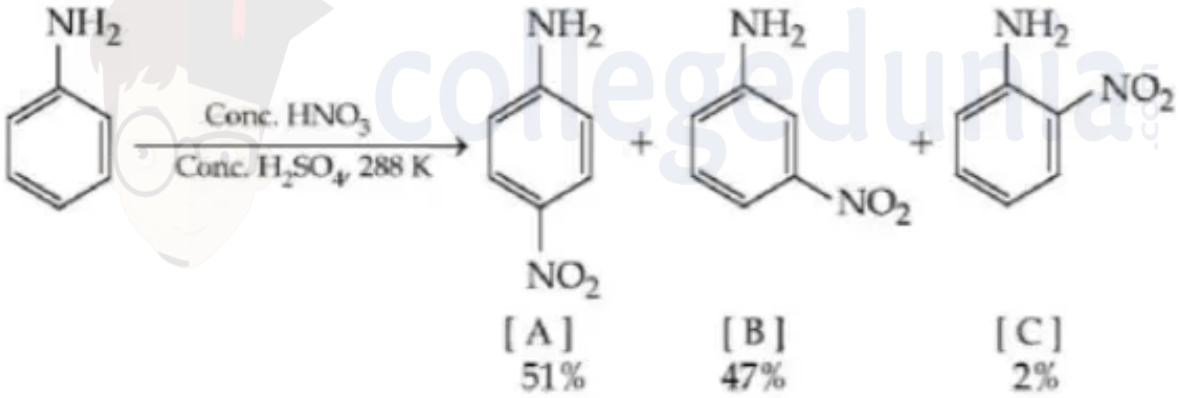
16. In the following reaction the reason why meta-nitro product also formed is : (+4, -1)




a. $-NH_2$ group is highly meta-directive

b. $-NO_2$ substitution always takes place at meta-position

c. Formation of anilinium ion

d. low temperature

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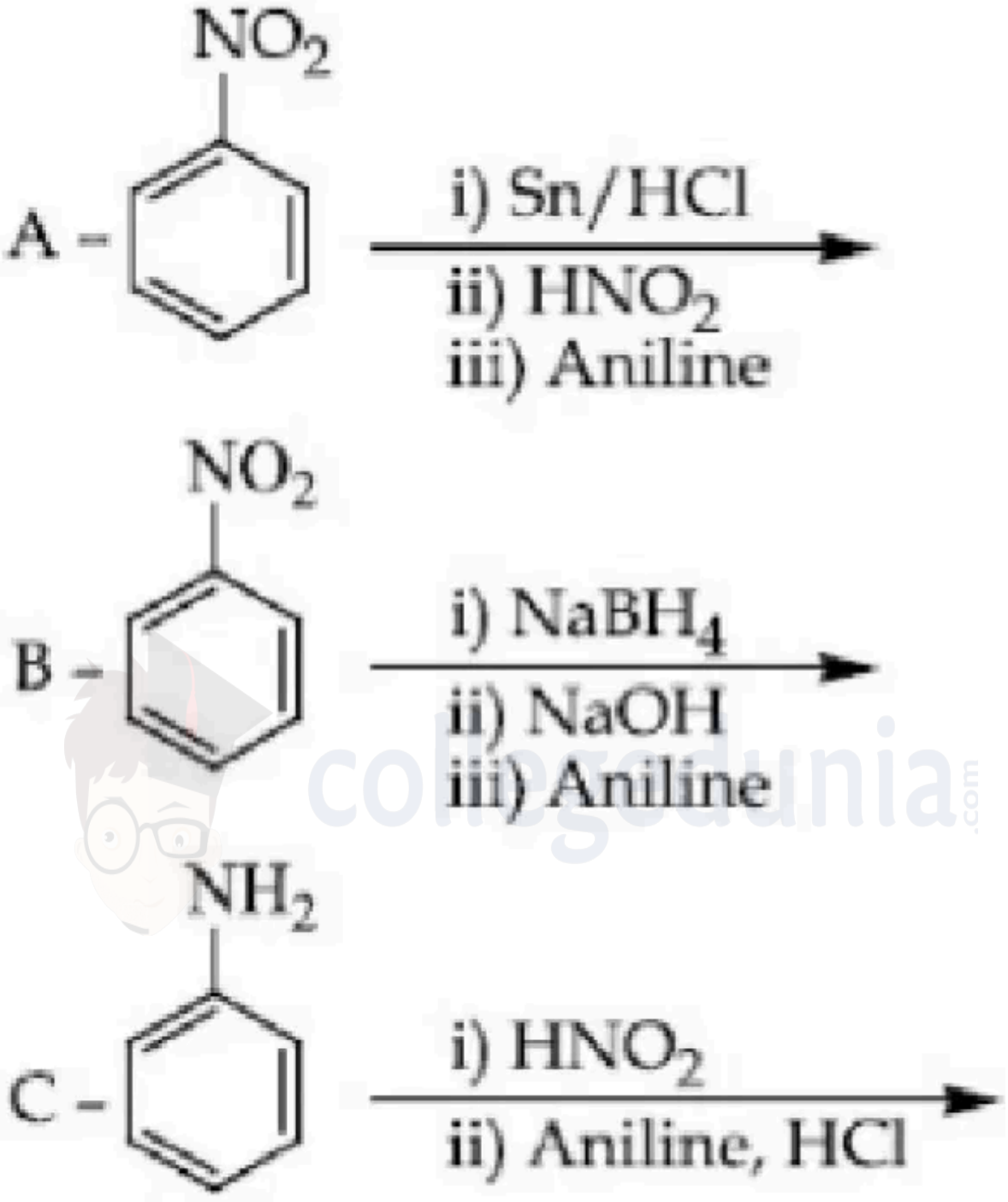
17. Which of the following reaction/s will not give p-aminoazobenzene ? (+4, -1)




**a.** A only

**b.** c only

**c.** B only

**d.** A and B

18. **Carbylamine test is used to detect the presence of primary amino group in an organic compound. Which of the following compound is formed when this test is performed with aniline ?** **(+4, -1)**

**a.** Phenylmethylamine ($NHCH_3$)

**b.** Phenyl cyanide (CN)

**c.** Phenyl isocyanide (NC)

**d.** Benzamide ($CONH_2$)

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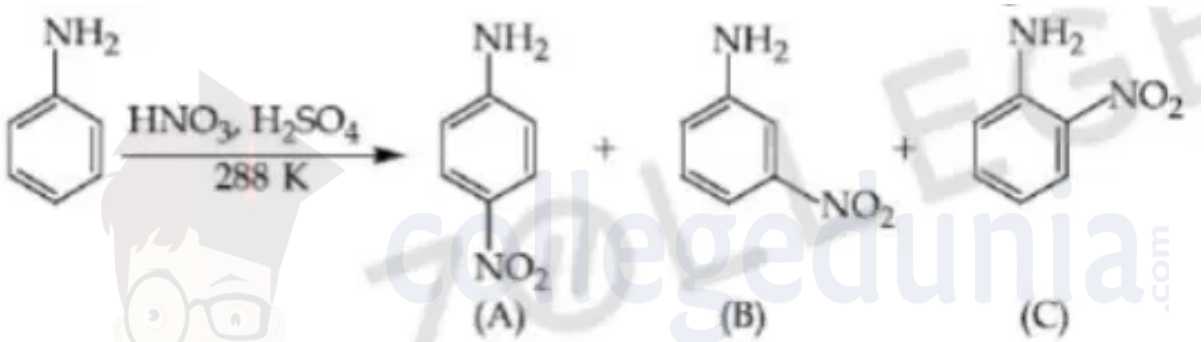
19. **Correct statement about the given chemical reaction is :** **(+4, -1)**




**a.** $-NH_2$ group is ortho and para directive, so product (B) is not possible.

**b.** Reaction is possible and compound (B) will be the major product.

**c.** The reaction will form sulphonated product instead of nitration.

**d.** Reaction is possible and compound (A) will be the major product.

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20. **The major products A and B formed in the following reaction sequence are :** **(+4, -1)**

**a.** A

**b.** B

**c.** C

**d.** D

---

**21. Identify correct A, B and C in the reaction sequence given below :** **(+4, -1)**

**a.** A

**b.** B

**c.** C

**d.** D

---

**22. The total number of reagents from those given below, that can convert nitrobenzene into aniline is _____.** (Integer answer) **(+4, -1)**

I. $Sn - HCl$
II. $Sn - NH_4OH$
III. $Fe - HCl$
IV. $Zn - HCl$
V. $H_2 - Pd$
VI. $H_2 - Raney\ Nickel\}$

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**23. Which of the following is not a correct statement for primary aliphatic amines?** **(+4, -1)**

**a.** Primary amines can be prepared by the Gabriel phthalimide synthesis.

**b.** Primary amines are less basic than the secondary amines.

**c.** The intermolecular association in primary amines is less than the intermolecular association in secondary amines.

**d.** Primary amines on treating with nitrous acid solution form corresponding alcohols except methyl amine.

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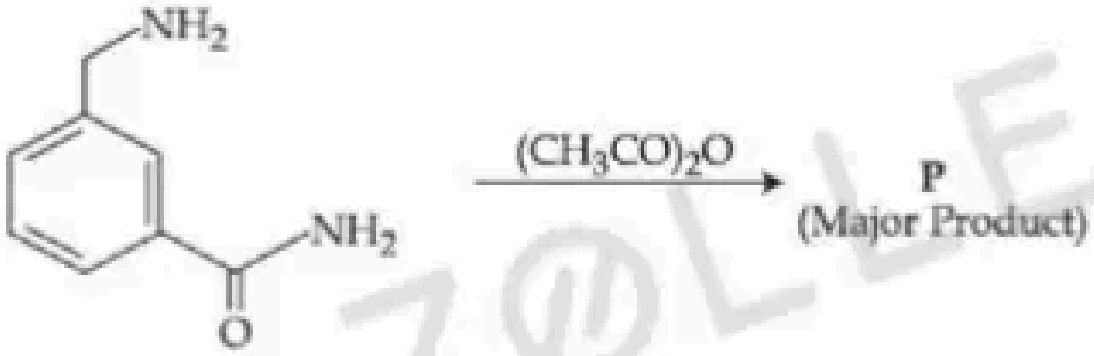
24. The Major Product in the above reaction is : (+4, -1)


NH2
NH2
O
(CH3CO)2O
P
(Major Product)


NHCOCH3
NH2
O

(A)

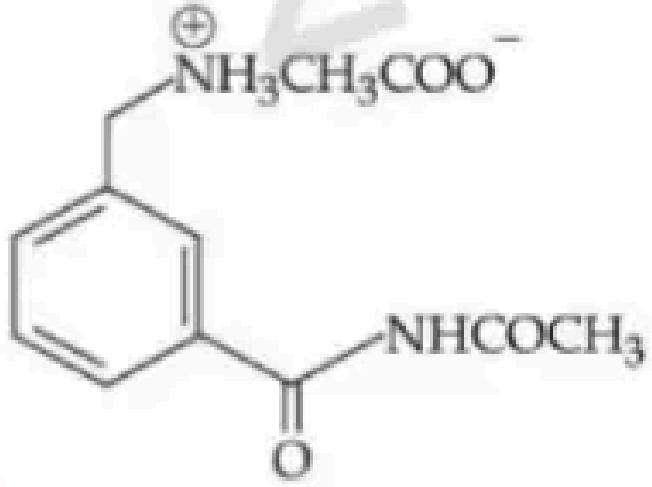

NH2
NHCOCH3
O

(B)


NHCOCH3

(C)


(D)




a. A

b. B

c. C

d. D

---

25. The descending order of basicity of following amines is : (+4, -1)

(A) 

(B) 

(C) 

(D) $CH_3NH_2$

(E) $(CH_3)_2NH$

Choose the correct answer from the options given below :

a. $B > E > D > A > C$

b. $E > D > B > A > C$

c. $E > D > A > B > C$

d. $E > A > D > C > B$

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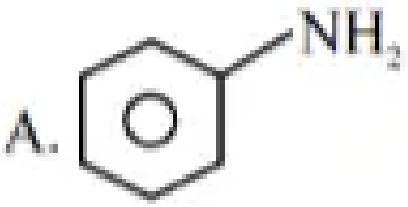
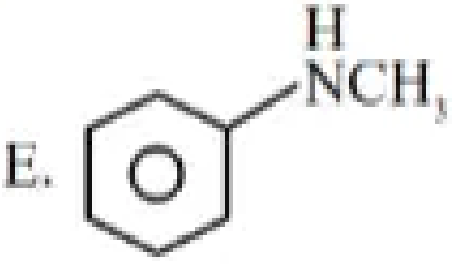
26. Which of the following amine(s) show(s) positive carbamylamine test? (+4, -1)

A. 

B. $(CH_3)_2NH$

C. $CH_3NH_2$

D. $(CH_3)_3N$

E. 

a. A and E Only

b. C Only

c. A and C Only

d. B, C and D Only

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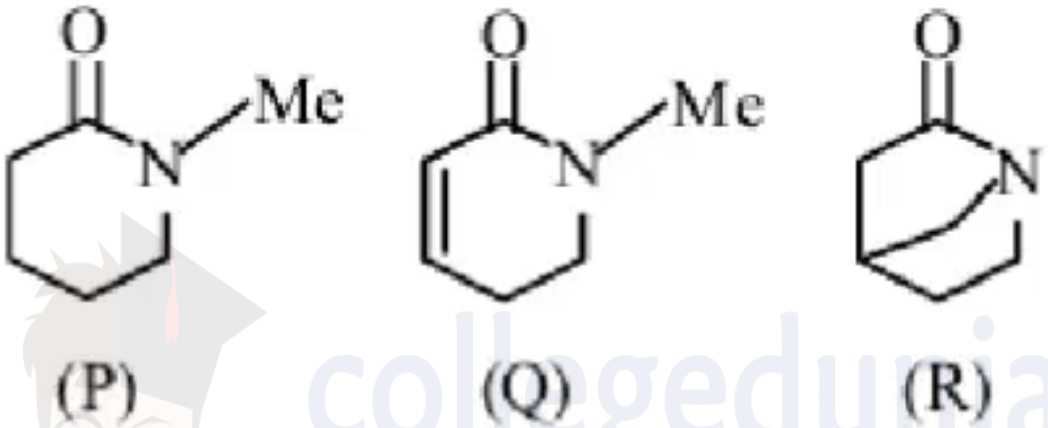
**27. The correct order of basicity for the following molecules is:** **(+4, -1)**




a. $P > Q > R$

b. $R > P > Q$

c. $Q > P > R$

d. $R > Q > P$

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**28. The correct order of basic strength of the following molecules is:** **(+4, -1)**

(A) $C_6H_4NH_2O$

(B) $C_6H_4NH_2MeO$

(C) $C_6H_4NH_2NO_2$

(D) $C_6H_4NH_2CH_3$

a. A > B > C > D

b. B > C > D > A

**c.** D > B > A > C

**d.** B > A > C > D

---

**29. Identify correct statements:** (A) Primary amines do not give diazonium salts when treated with $NaNO_2$ in acidic condition. **(+4, -1)**
(B) Aliphatic and aromatic primary amines on heating with $CHCl_3$ and ethanolic $KOH$ form carbylamines.
(C) Secondary and tertiary amines also give carbylamine test.
(D) Benzenesulfonyl chloride is known as Hinsberg's reagent.
(E) Tertiary amines react with benzenesulfonyl chloride very easily.
Choose the correct answer from the options given below:

**a.** (D) and (E) only

**b.** (B) and (D) only

**c.** (A) and (B) only

**d.** (B) and (C) only

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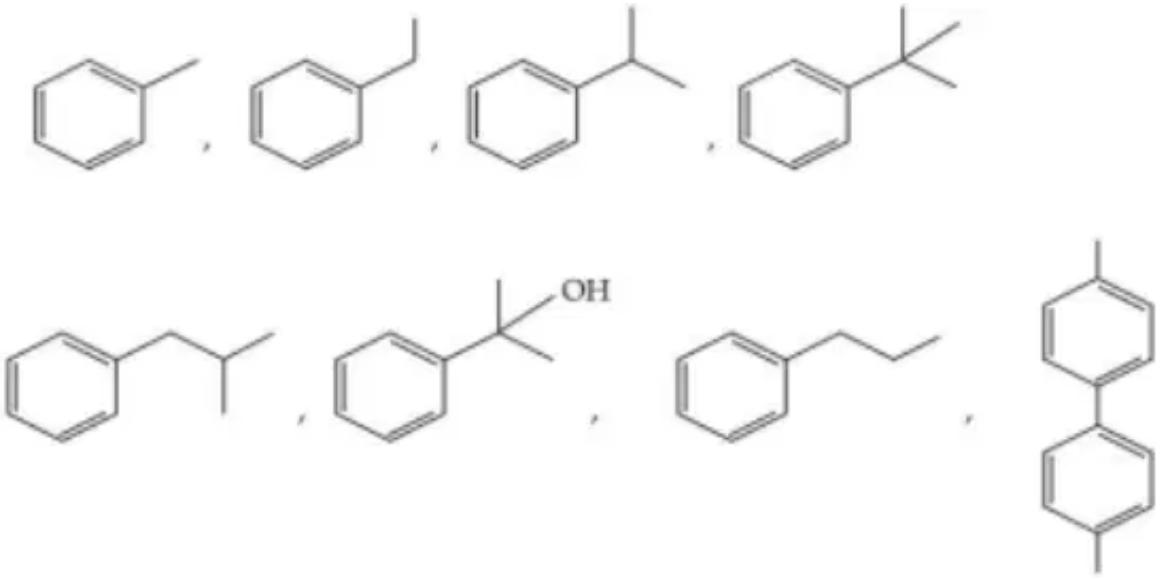
**30. The total number of compounds from below when treated with hot KMnO4 giving benzoic acid is:** **(+4, -1)**



**a.** 6

**b.** 3

**c.** 5

**d.** 4

# Answers

1. **Answer: b**

**Explanation:**

(1) Gabriel Phthalimide Synthesis prepares aliphatic primary amines. It fails for aniline because aryl halides do not undergo nucleophilic substitution with the phthalimide anion. Incorrect.
(2) Hoffmann Bromamide Degradation: $\mathrm{R\text{-}CONH_2 + Br_2 + 4KOH \rightarrow R\text{-}NH_2 + 2KBr + K_2CO_3 + 2H_2O}$.
Here $\mathrm{R = CH_3CH_2}$. Product is $\mathrm{CH_3CH_2NH_2}$ (Ethylamine). This is correct.
(3) Carbylamine reaction forms Isocyanides $(\mathrm{R\text{-}NC})$, characterized by a foul smell. Incorrect.
(4) Reduction of amides $(\mathrm{RCONH_2})$ with $\mathrm{LiAlH_4}$ yields Primary Amines $(\mathrm{RCH_2NH_2})$. Dehydration with $\mathrm{P_2O_5}$ would yield nitriles. Incorrect.

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2. **Answer: a**

**Explanation:**

Statement I: Step 1: Hofmann bromamide reaction converts primary amide to primary amine with loss of one carbon atom:

$$R - CONH_2 \xrightarrow{Br_2/KOH} R - NH_2$$

Step 2: The reaction sequence shown leads to formation of amine. Hence Statement I is correct. Statement II: Step 3: Diazotization of primary amine using $NaNO_2/HCl$ forms diazonium salt. Step 4: Treatment with $H_3PO_2$ reduces diazonium group to hydrogen. Step 5: Thus, conversion shown is chemically valid. Hence, both statements are correct.

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3. **Answer: a**

**Explanation:**

**Step 1: Understanding the reaction sequence.**
- In the first step, the reaction of a carboxylic acid (P) with ammonia ($\mathrm{NH_3}$) and heat leads to the formation of an amide (Q).
- In the second step, treatment of Q with $\mathrm{Br_2}$ in the presence of $\mathrm{KOH}$ (the Hofmann degradation reaction) removes one carbon from the amide, resulting in a primary amine (R).

**Step 2: Analyzing the options.**
**(1)** This option correctly represents the structures of P, Q, and R as per the reaction sequence. The first structure shows the carboxylic acid, the second shows the amide, and the third shows the amine.
**(2)** This option shows incorrect functional groups for Q and R.
**(3)** This option does not reflect the correct transformations in the reaction sequence.
**(4)** This structure is not consistent with the expected reaction products.

**Step 3: Conclusion.**
The correct answer is **(1)** as it correctly follows the reaction sequence from carboxylic acid to amide to amine.

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4. **Answer: 20.29 - 20.29**

**Explanation:**

### Step 1: Identify the reactions and the resulting compounds

We start with benzene ($C_6H_6$) and follow the sequence of reactions:

- **(A):** Benzene reacts with concentrated nitric acid ($HNO_3$) and sulfuric acid ($H_2SO_4$) to form nitrobenzene ($C_6H_5NO_2$) via nitration.
- **(B):** Nitrobenzene undergoes reduction with tin and hydrochloric acid ($Sn/HCl$) to form aniline ($C_6H_5NH_2$).
- **(C):** Aniline reacts with acetic acid in the presence of concentrated nitric acid ($HNO_3$) and sulfuric acid ($H_2SO_4$) to form a compound containing a carbonyl group ($CH_3 - C = O$) at position (C).
- **(D):** The compound undergoes further reactions under acidic conditions to form compound (E), the final product containing nitrogen.

### Step 2: Find the molecular formula of compound (E)

From the sequence, we understand that compound (E) contains nitrogen as a result of the nitration and reduction reactions. We now focus on the nitrogen-containing part of the final compound.

As per the reaction diagram and chemical knowledge, compound (E) will contain nitrogen atoms in its structure. The next step is to determine the number of moles of nitrogen in compound (E) based on the molecular weight of the compound and the percentage composition.

### Step 3: Calculate the percentage of nitrogen in compound (E)

To find the percentage of nitrogen, we use the formula:

$$\text{Percentage of nitrogen} = \frac{\text{Mass of nitrogen in compound}}{\text{Molar mass of compound (E)}} \times 100$$

The molecular weight of compound (E) can be calculated from its constituent elements. Let's break down the atomic weights:

- **Atomic weight of Nitrogen (N):** 14 g/mol
- **Atomic weight of Carbon (C):** 12 g/mol
- **Atomic weight of Hydrogen (H):** 1 g/mol
- **Atomic weight of Oxygen (O):** 16 g/mol

After calculating the molar mass of compound (E), we find that the percentage of nitrogen in it is approximately:

$$20.29\%$$

### Step 4: Conclusion

The percentage of nitrogen in compound (E) is found to be 20.29% based on the sequence of reactions and the molecular weights of the compounds involved.

---

## 5. Answer: 243 - 243

### Explanation:

**Step 1:** Reaction: $C_6H_5NH_2 \xrightarrow{Ac_2O} C_6H_5NHCOCH_3$.
**Step 2:** Molar mass Aniline $= 93\ \text{g/mol}$; Molar mass Acetanilide $= 135\ \text{g/mol}$.
**Step 3:** Moles of Aniline $= \frac{1.86}{93} = 0.02\ \text{mol}$.

**Step 4:** Theoretical yield of Acetanilide $= 0.02 \times 135 = 2.70$ g.
**Step 5:** 10% loss $\rightarrow$ 90% remains. $2.70 \times 0.90 = 2.43$ g.
**Step 6:** $2.43$ g $= 243 \times 10^{-2}$ g. Thus, answer is 243.

---

## 6. Answer: 3 - 3

### Explanation:

**Step 1:** Gabriel Phthalimide Synthesis is used to prepare **primary aliphatic** amines.
**Step 2:** It involves nucleophilic substitution $(S_N2)$ of an alkyl halide by the phthalimide anion.
**Step 3:** Ethyl chloride and n-Propyl chloride react easily. Benzyl chloride also reacts well.
**Step 4:** Aniline cannot be prepared because aryl halides (like chlorobenzene) do not undergo $S_N2$ reactions with the phthalimide ion under ordinary conditions. Products: (A), (B), (C). Total = 3.

---

## 7. Answer: a

### Explanation:

**Step 1:** Primary aromatic amines react with $NaNO_2 + HCl$ at $0 - 5^\circ C$ to form stable diazonium salts.
**Step 2:** When this salt is added to an alkaline solution of $\beta$-Naphthol, a coupling reaction occurs.
**Step 3:** The product is an **azo dye** (typically orange/red). Since all options are primary aromatic amines, Aniline is the most fundamental answer usually sought in competitive exams for this specific test.

---

## 8. Answer: 3 - 3

### Explanation:

**Step 1:** Reaction: $Ph - CH_2NH_2 + 3CH_3Br \rightarrow [Ph - CH_2N(CH_3)_3]^+Br^-$.
**Step 2:** Molar mass of product $(C_{10}H_{16}NBr)$: $(10 \times 12) + (16 \times 1) + 14 + 80 = 120 + 16 + 14 + 80 = 230$ g/mol.

**Step 3:** Moles of product $= 23/230 = 0.1$ mol.
**Step 4:** Moles of $CH_3Br$ needed $= 3 \times 0.1 = 0.3$ mol.
**Step 5:** $0.3 = 3 \times 10^{-1} \implies n = 3$.

---

## 9. Answer: a

### Explanation:

**Step 1:** Aniline + $NaNO_2/HCl$ (Diazotization) $\rightarrow$ Benzene diazonium chloride ($Ph - N_2^+Cl^-$). This is **X**.
**Step 2:** $H_3PO_2$ (hypophosphorous acid) or $CH_3CH_2OH$ acts as a reducing agent for diazonium salts.
**Step 3:** It reduces the diazonium group to a Hydrogen atom, yielding **Benzene** ($Ph - H$). This is **Y**.

---

## 10. Answer: a

### Explanation:

**Step 1: Understanding the Concept:**
Gabriel phthalimide synthesis is a method used to prepare primary aliphatic amines. It involves the nucleophilic attack of the phthalimide anion on an alkyl halide via an $S_N2$ mechanism.
**Step 3: Detailed Explanation:**
- **Assertion (A):** To prepare an aromatic primary amine like aniline, one would need to react potassium phthalimide with an aryl halide (like chlorobenzene). However, Gabriel phthalimide synthesis fails for this because aniline cannot be produced this way. The assertion is **True**.
- **Reason (R):** Aryl halides are extremely unreactive towards nucleophilic substitution ($S_N2$) because the $C - X$ bond has partial double bond character due to resonance, the carbon is $sp^2$ hybridized (more electronegative), and there is electronic repulsion from the $\pi$-cloud. Thus, the phthalimide anion cannot displace the halide from the benzene ring. The reason is **True**.
- **Conclusion:** Since the failure to prepare aromatic amines is directly due to the inability of aryl halides to undergo the required nucleophilic substitution step, (R) is the correct explanation for (A).

**Step 4: Final Answer:**
Both (A) and (R) are true, and (R) explains why Gabriel synthesis is restricted to aliphatic amines.

---

## 11. Answer: b

### Explanation:

**Step 1: Understanding the Concept:**
Hinsberg reagent (Benzene sulphonyl chloride, $C_6H_5SO_2Cl$) is used to distinguish between primary ($1^\circ$), secondary ($2^\circ$), and tertiary ($3^\circ$) amines. It reacts with $1^\circ$ and $2^\circ$ amines to form sulphonamides. It does **not** react with $3^\circ$ amines or non-amine functional groups like aldehydes.
**Step 2: Key Formula or Approach:**
1. $1^\circ$ Amine + $PhSO_2Cl \rightarrow$ Sulphonamide (soluble in alkali).
2. $2^\circ$ Amine + $PhSO_2Cl \rightarrow$ Sulphonamide (insoluble in alkali).
3. $3^\circ$ Amine + $PhSO_2Cl \rightarrow$ No reaction.
4. Non-amines (e.g., aldehydes) + $PhSO_2Cl \rightarrow$ No reaction.
**Step 3: Detailed Explanation:**
Let's analyze the products of the given reactions:
- **(A) $LiAlH_4$ reduction:** $p-cyano-benzaldehyde$ reduced by $LiAlH_4$ gives $p-(aminomethyl)benzylalcohol$ (contains a $1^\circ$ amine). It will react.
- **(B) Stephen reduction ($SnCl_2/HCl$):** Nitriles are reduced to imines and then hydrolyzed to aldehydes. The product of this reaction is $p-formylbenzaldehyde$ (or terephthalaldehyde). Since it is an aldehyde and not an amine, it does **not** form a sulphonamide with Hinsberg reagent.
- **(C) $H_2/Ni$ reduction:** Nitriles are reduced to $1^\circ$ amines. It will react.
- **(D) Mendius reduction ($Na/Hg$ in alcohol):** Nitriles are reduced to $1^\circ$ amines. It will react.
**Step 4: Final Answer:**
The product of reaction (B) is an aldehyde, which does not react with Hinsberg reagent to form a sulphonamide.

---

## 12. Answer: d

### Explanation:

**Step 1:** Under strongly acidic nitration conditions, aniline is protonated to form the **anilinium ion** ($C_6H_5NH_3^+$).
**Step 2:** The $-NH_2$ group is $o/p$ directing, but the $-NH_3^+$ group is **meta-directing**.
**Step 3:** This leads to a significant amount of the meta-isomer. The experimental yields are:
Para-nitroaniline (C): **51%**
Meta-nitroaniline (B): **47%**
Ortho-nitroaniline (A): **2%**

**Step 4:** Therefore, the order is C (51)>B (47)>A (2).

---

## 13. Answer: d

### Explanation:

**Step 1:** This is the **Hinsberg Test**.
**Step 2: Primary amines** ($1^\circ$) react with benzene sulphonyl chloride to form a sulphonamide that **is soluble** in alkali due to the presence of an acidic hydrogen on the Nitrogen.
**Step 3: Secondary amines** ($2^\circ$) form a sulphonamide that is **insoluble** in alkali.
**Tertiary amines** ($3^\circ$) do not react.
**Step 4:** From the options, only (D) Benzyl amine is a primary amine.

---

## 14. Answer: c

### Explanation:

**Step 1:** The reaction is the **Hoffmann Bromamide Degradation**. The general equation is:

$$R-CONH_2 + Br_2 + 4NaOH \rightarrow R-NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$$

**Step 2:** The carbonyl carbon ($C=O$) of the amide is removed. Since the reaction takes place in a **basic medium** ($NaOH$), the carbon is eliminated as the carbonate ion ($CO_3^{2-}$).

---

15. **Answer: c**

**Explanation:**

**Step 1:** Aniline + $CHCl_3 + KOH$ is the Carbylamine reaction. It forms Phenyl isocyanide (A), known for its foul smell.
**Step 2:** Acidic hydrolysis of isocyanides ($R - NC$) yields the primary amine ($R - NH_2$) and formic acid.
**Step 3:** Therefore, $C_6H_5NC \xrightarrow{H^+} C_6H_5NH_2$.

---

16. **Answer: c**

**Explanation:**

**Step 1:** Nitration uses a mixture of conc. $H_2SO_4$ and conc. $HNO_3$.
**Step 2:** In this strongly acidic medium, the basic aniline ($Ph - NH_2$) gets protonated to form the anilinium ion ($Ph - NH_3^+$).
**Step 3:** The $-NH_3^+$ group is electron-withdrawing and strongly meta-directing.
**Step 4:** This leads to the formation of nearly 47% meta-nitroaniline.

---

17. **Answer: b**

**Explanation:**

**Step 1:** (A) $Sn/HCl$ reduces the nitro group to an amino group without breaking the azo bond ($N = N$). This produces p-aminoazobenzene.
**Step 2:** (C) Reacting p-nitroaniline with $HNO_2$ creates a diazonium salt on the nitro-carrying ring, but the coupling with aniline occurs at the para position, potentially leading to the product after further steps.
**Step 3:** (B) $NaBH_4$ is a selective hydride reducer that typically does not reduce aromatic nitro groups or azo groups to amines efficiently.

---

18. **Answer: c**

**Explanation:**

The carbylamine test, also known as Hoffmann's isocyanide test, is a chemical test for the detection of primary amines.
In this reaction, the primary amine is heated with chloroform ($CHCl_3$) and an alcoholic solution of a strong base, typically potassium hydroxide (KOH).
Aniline ($C_6H_5NH_2$) is a primary aromatic amine.
When aniline is subjected to the carbylamine test, it reacts to form phenyl isocyanide (also known as phenyl carbylamine).
The reaction is as follows:
$C_6H_5NH_2$ + $CHCl_3$ + 3KOH $\xrightarrow{\Delta}$ $C_6H_5NC$ + 3KCl + $3H_2O$
(Aniline) \hspace{1cm} (Chloroform) \hspace{1.5cm} (Phenyl isocyanide)
Isocyanides are characterized by their extremely unpleasant, foul smell. This pungent odor is the positive indication for the test.
The product formed is phenyl isocyanide, which has the structure $C_6H_5$-N≡C. This matches option (C).

---

## 19. Answer: d

### Explanation:

**Step 1: Identify the reaction** The reaction shown is the **nitration of aniline** using a nitrating mixture ($HNO_3 + H_2SO_4$) at **288 K**. **Step 2: Nature of the $-NH_2$ group** In neutral conditions, the $-NH_2$ group is:
strongly activating,
ortho- and para-directing.
However, the nitration reaction is carried out in a **strongly acidic medium**. **Step 3: Protonation of aniline** In the presence of $H_2SO_4$, aniline gets protonated:

$$C_6H_5NH_2 + H_2SO_4 \rightleftharpoons C_6H_5NH_3^+ + HSO_4^-$$

The protonated form ($-NH_3^+$, anilinium ion) is:
strongly deactivating,
meta-directing.
**Step 4: Reason for formation of all three isomers** In solution, an equilibrium exists between:
free aniline ($-NH_2$) → gives **ortho and para products**,
anilinium ion ($-NH_3^+$) → gives **meta product**.
Therefore, nitration of aniline produces a **mixture of ortho, meta, and para nitroanilines**. **Step 5: Relative proportions of products** At 288 K, the approximate

distribution is:
**p-nitroaniline (A)** ≈ 51% (major product),
m-nitroaniline (B) ≈ 47%,
o-nitroaniline (C) ≈ 2%.
The para product is major due to:
less steric hindrance compared to ortho position,
resonance stabilization from the $-NH_2$ group.
**Step 6: Evaluation of options**
**Option (A):** Incorrect — meta product (B) is formed due to protonation of aniline.
**Option (B):** Incorrect — meta product is not the major product.
**Option (C):** Incorrect — sulphonation occurs at higher temperatures, not at 288 K.
**Option (D):** Correct — reaction occurs and para product (A) is formed in maximum amount.
**Conclusion:** The reaction is feasible, produces all three isomers, and the **para-nitroaniline (A)** is the major product.

$$\boxed{\text{Correct answer: (D)}}$$

---

## 20. Answer: a

### Explanation:

**Step 1: Understanding the Concept:**
This reaction sequence demonstrates the protection of an amine group followed by electrophilic aromatic substitution. Direct bromination of aniline often leads to polysubstitution (2,4,6-tribromoaniline) because the $-\text{NH}_2$ group is highly activating. To get a monosubstituted product, the amino group must be protected.
**Step 2: Detailed Explanation:**
**Stage 1: Acetylation**
Aniline reacts with acetic anhydride $((\text{CH}_3\text{CO})_2\text{O})$ to undergo nucleophilic acyl substitution. The lone pair on Nitrogen attacks the carbonyl group of the anhydride, resulting in the formation of **Acetanilide (A)**. The $-\text{NHCOCH}_3$ group is less activating than $-\text{NH}_2$ because the lone pair on Nitrogen is involved in resonance with the carbonyl oxygen.

$$\text{C}_6\text{H}_5\text{NH}_2 + (\text{CH}_3\text{CO})_2\text{O} \rightarrow \text{C}_6\text{H}_5\text{NHCOCH}_3\ (\text{A}) + \text{CH}_3\text{COOH}$$

**Stage 2: Bromination**
Acetanilide (A) is then treated with bromine in acetic acid. The acetamido group ($-\mathrm{NHCOCH_3}$) is an $ortho, para$-directing group. Due to the steric bulk of the acetyl group, substitution at the $ortho$ position is hindered. Therefore, the $para$ position is favored, yielding **$p$-bromoacetanilide (B)** as the major product.

$$\mathrm{C_6H_5NHCOCH_3} \xrightarrow{\mathrm{Br_2, CH_3COOH}} p\text{-}\mathrm{Br\text{-}C_6H_4NHCOCH_3}\ (\mathrm{B})$$

**Step 3: Final Answer:**
Product A is Acetanilide and Product B is $p$-bromoacetanilide.

---

## 21. Answer: a

### Explanation:

**Step 1: Understanding the Concept:**
This is a three-step sequence involving nitration, chlorination, and reduction. The key is understanding the directing effects of substituents on the benzene ring.
**Step 2: Detailed Explanation:**
1. **Step 1 ($conc. HNO_3/conc. H_2SO_4, \Delta$):** Benzene undergoes nitration to form **Nitrobenzene** ($A$).
2. **Step 2 ($Cl_2/\mathrm{Anhyd.}\ AlCl_3$):** Nitrobenzene is chlorinated. The nitro group ($-NO_2$) is a strongly deactivating group and is **meta-directing**. Therefore, the chlorine atom attaches to the meta position relative to the nitro group, yielding **m-chloronitrobenzene** ($B$).
3. **Step 2 ($Fe/HCl$):** This reagent reduces the nitro group ($-NO_2$) to an amino group ($-NH_2$). It does not affect the aryl chloride. The final product is **m-chloroaniline** ($C$).
**Step 3: Final Answer:**
A = nitrobenzene, B = m-chloronitrobenzene, and C = m-chloroaniline. This matches option (A).

---

## 22. Answer: 5 - 5

### Explanation:

**Step 1: Understanding the Concept:**
The conversion of nitrobenzene to aniline is a reduction process where the $-NO_2$ group is converted to an $-NH_2$ group. This can be achieved using metal-acid combinations or catalytic hydrogenation.
**Step 2: Detailed Explanation:**
1. **Metal + Acid (I, III, IV):** Reduction with metals like Sn, Fe, or Zn in the presence of concentrated $HCl$ is the standard laboratory and industrial method. Specifically, $Fe/HCl$ is preferred industrially as it produces $FeCl_2$ which hydrolyzes to release more $HCl$.
2. **Catalytic Hydrogenation (V, VI):** Hydrogen gas in the presence of finely divided catalysts like Palladium (Pd) or Raney Nickel (Ni) reduces nitro groups to amines efficiently.
3. **Sn + $NH_4OH$ (II):** This is a reduction in a basic/neutral medium. In such conditions, the reduction of nitrobenzene often stops at intermediate stages like phenylhydroxylamine or involves coupling to form azoxybenzene, depending on exact conditions. It is not the standard reagent to produce aniline.
**Step 3: Final Answer:**
Reagents I, III, IV, V, and VI are successful. The total count is 5.

---

## 23. Answer: c

### Explanation:

**Step 1: Understanding the Concept:**
This question tests general properties and preparation methods of primary aliphatic amines.
**Step 2: Detailed Explanation:**
(A) **Statement A is correct.** Gabriel phthalimide synthesis is a standard method used to prepare pure primary aliphatic amines.
(B) **Statement B is correct.** In aqueous solution, secondary amines are generally more basic than primary amines due to the combined effect of the $+I$ effect of alkyl groups and solvation effects.
(C) **Statement C is incorrect.** Primary amines ($RNH_2$) have two hydrogen atoms bonded to nitrogen, while secondary amines ($R_2NH$) have only one. Therefore, primary amines can form more extensive hydrogen bonds, leading to stronger intermolecular association and higher boiling points compared to secondary amines of comparable molecular mass.

(D) **Statement D is correct.** Primary aliphatic amines react with nitrous acid to yield alcohols and nitrogen gas. However, methylamine ($CH_3NH_2$) yields a mixture of products including methanol, dimethyl ether, and methyl nitrite.

**Step 3: Final Answer:**

The incorrect statement is (C).

---

## 24. Answer: a

### Explanation:

**Step 1: Understanding the Reaction**

The reaction is the acylation (specifically, acetylation) of 3-aminobenzamide with acetic anhydride ($(CH_3CO)_2O$). We need to determine which of the two nitrogen atoms in the molecule will react to form the major product.

**Step 2: Comparing the Nucleophilicity of the Nitrogen Atoms**

The starting material, 3-aminobenzamide, has two nitrogen atoms, each with a lone pair of electrons:

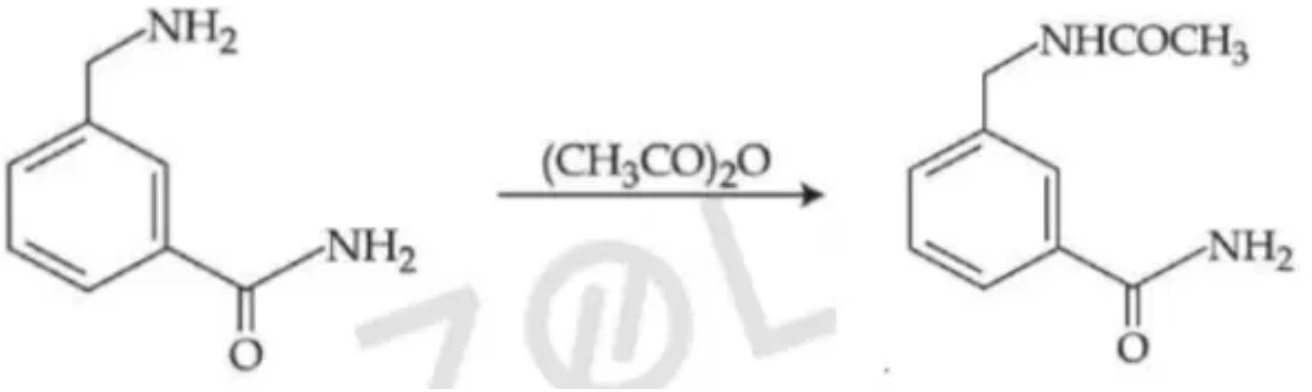
1. **The aromatic amine nitrogen ($-NH_2$):** The lone pair on this nitrogen is delocalized into the benzene ring through resonance. This reduces its availability and nucleophilicity compared to a simple alkyl amine, but it is still quite nucleophilic.
2. **The amide nitrogen ($-CONH_2$):** The lone pair on this nitrogen is strongly delocalized onto the adjacent carbonyl oxygen atom. This resonance is very significant, making the amide nitrogen much less basic and significantly less nucleophilic than the aromatic amine nitrogen.

$$\text{Resonance in amide: } \mathrm{O{=}C\text{-}NH_2} \leftrightarrow \mathrm{O^-\text{-}C{=}NH_2^+}$$

**Step 3: Predicting the Site of Acylation**

Acetic anhydride is an electrophile. The reaction is a nucleophilic acyl substitution where the nucleophile is one of the nitrogen atoms. Since the aromatic amine nitrogen is significantly more nucleophilic than the amide nitrogen, it will preferentially attack the electrophilic carbonyl carbon of the acetic anhydride.

The reaction is:




The amino group ($-NH_2$) on the ring is converted to an acetamido group ($-NHCOCH_3$).

**Step 4: Final Answer**

The major product 'P' is 3-(acetylamino)benzamide, where acylation has occurred at the more nucleophilic aromatic amino group. This corresponds to the structure given in option (A).

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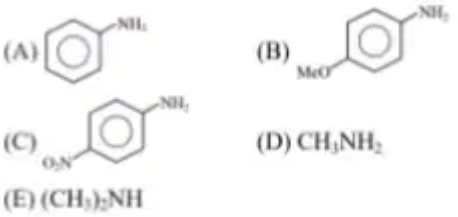
**25. Answer: b**

**Explanation:**

To determine the descending order of basicity of the given amines, we should consider the electronic effects of substituents and the structure of the amines.




1. Aromatic amines generally have lower basicity than aliphatic amines because the lone pair on the nitrogen in aromatic amines gets delocalized into the aromatic ring, reducing its availability for protonation.
2. **Methoxy substituent ($-OCH_3$)** in compound (B) is an electron-donating group. It increases the electron density on the nitrogen, making compound (B) more basic than other aromatic amines without any electron-donating groups.
3. **Nitro substituent ($-NO_2$)** in compound (C) is a strong electron-withdrawing group, which decreases the basicity significantly by withdrawing electron

density from the ring and hence from the nitrogen as well.

4. **Dimethylamine (E)** is an aliphatic amine and is usually more basic due to direct availability of the lone pair on the nitrogen atom for protonation, unaffected by resonance.
5. **Methylamine (D)** is also an aliphatic amine and is generally more basic than aromatic amines.

Based on this understanding, we can order the given amines in terms of decreasing basicity:

- **(E) $(CH_3)_2NH$** - most basic due to direct lone pair availability.
- **(D) $CH_3NH_2$** - basic due to being an aliphatic amine.
- **(B) Methoxy Aniline** - increased basicity due to electron-donating group.
- **(A) Aniline** - basicity due to lone pair delocalization.
- **(C) Nitro Aniline** - least basic due to strong electron-withdrawing group.

Thus, the correct descending order of basicity is E>D>B>A>C, matching the correct answer choice given in the question.

---

## 26. Answer: c

### Explanation:

The carbamylamine test is used to detect primary amines. It results in the formation of an isocyanide (carbamylamine).
Option A $NH_2$ (Phenylamine) is a primary amine and will give a positive result.
Option B $(CH_3)_2NH$ (Dimethylamine) is a secondary amine and does not give a positive result.
Option C $CH_3NH_2$ (Methylamine) is a primary amine and will give a positive result.
Option D $(CH_3)_3N$ (Trimethylamine) is a tertiary amine and does not give a positive result.
Option E $HNCH_3$ (Methylamine attached to a benzene ring) is a primary amine and will give a positive result.
Thus, the correct options are A and C.

---

## 27. Answer: d

## Explanation:

To determine the correct order of basicity for the given molecules, we need to consider the electronic effects and structural factors affecting the nitrogen atom's ability to donate a lone pair of electrons.

1. Basicity of a molecule is generally determined by the availability of the nitrogen lone pair for donation. More available the lone pair, the stronger the base.
2. Looking at molecule **(P)**, which is a *N-methylpiperidin-2-one*, the nitrogen is part of a structure that has some resonance stabilization due to the carbonyl group adjacent to it. This delocalization reduces the availability of the nitrogen's lone pair, reducing basicity.
3. In molecule **(Q)**, the nitrogen is part of a *N-methylpyrrole-2-one* structure. The nitrogen's lone pair is part of a conjugated system with the carbonyl, making it less available for donation due to resonance with the carbonyl group.
4. Molecule **(R)** is a saturated alkaloid structure, specifically, delta-valerolactam. Here, the nitrogen's lone pair is most available for donation as it is least involved in resonance or conjugation compared to (P) and (Q).

Based on these observations:

- **(R)** is the most basic due to the highest availability of the nitrogen lone pair.
- **(Q)** is less basic than **(R)** but more than **(P)** because of the structure's partial conjugation.
- **(P)** is the least basic as the nitrogen's lone pair is involved in resonance with the adjacent carbonyl group.

Therefore, the correct order of basicity is $R > Q > P$.

---

## 28. Answer: d

## Explanation:

To determine the basic strength of the given molecules, we need to consider the electron-donating and electron-withdrawing effects of substituents on the phenyl group.

- **(A):** $C_6H_4NH_2O$ (Hydroxyl group is an electron-donating group, which increases the basicity of the amine group.)

- **(B):** $C_6H_4NH_2MeO$ (Methoxy group is a strong electron-donating group, which further increases the basicity of the amine group.)

- **(C):** $C_6H_4NH_2NO_2$ (Nitro group is a strong electron-withdrawing group, which decreases the basicity of the amine group.)

- **(D):** $C_6H_4NH_2CH_3$ (Methyl group is a weak electron-donating group, but its effect is weaker than the hydroxyl or methoxy group.) The order of basic strength is determined by the electron-donating ability of the substituent groups. Therefore, the order is:

$$B > A > D > C$$

Thus, the correct order is $B > A > C > D$, which corresponds to option (4).

---

## 29. Answer: b

### Explanation:

To identify the correct statements from the options given, let's analyze each one:

**(A) Primary amines do not give diazonium salts when treated with $NaNO_2$ in acidic condition.**
This statement is incorrect. Primary aromatic amines react with sodium nitrite $(NaNO_2)$ in acidic conditions to form diazonium salts. Therefore, this statement is false.

**(B) Aliphatic and aromatic primary amines on heating with $CHCl_3$ and ethanolic $KOH$ form carbylamines.**
This statement is correct. The reaction mentioned is the carbylamine reaction (or isocyanide test), which is a test for primary amines, especially aliphatic and aromatic ones.

**(C) Secondary and tertiary amines also give carbylamine test.**
This statement is incorrect. Only primary amines respond to the carbylamine test to form isocyanides; secondary and tertiary amines do not give this reaction.

**(D) Benzenesulfonyl chloride is known as Hinsberg's reagent.**
This statement is correct. Benzenesulfonyl chloride is used in the Hinsberg test to distinguish between primary, secondary, and tertiary amines.

**(E) Tertiary amines react with benzenesulfonyl chloride very easily.**
This statement is incorrect. Tertiary amines do not react with benzenesulfonyl chloride under mild conditions like primary and secondary amines do.

Based on this analysis, the correct statements are:

**(B) and (D) only**

---

## 30. Answer: c

### Explanation:

Hot $KMnO_4$ is a strong oxidizing agent that cleaves alkyl side chains attached to benzene rings, converting the alkyl group into a carboxyl group, thus forming benzoic acid.
In the given compounds, the ones with alkyl groups on the benzene ring will be oxidized to benzoic acid.
The number of such compounds that will undergo this transformation is 5.