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# Organic Compounds Containing Nitrogen — JEE (Main) Pattern Topic Test

FREE SAMPLE TEST · CHEMISTRY · PATTERN OF JEE (MAIN)

| DURATION | MAXIMUM MARKS | QUESTIONS | NAME / ROLL NO. |
|---|---|---|---|
| 60 minutes | 100 | 25 (20 + 5) | |

## GENERAL INSTRUCTIONS

1. This question paper has two sections, A and B. All 25 questions are compulsory.
2. Section A has TWENTY (20) multiple-choice questions. Each has FOUR options, (1), (2), (3) and (4), of which ONLY ONE is correct.
3. Section B has FIVE (05) questions whose answer is a numerical value. Enter the value rounded off to the nearest integer.
4. Marking scheme for both sections: +4 for a correct answer, −1 for an incorrect answer, 0 if the question is not attempted.
5. Use of a calculator, log tables or any other aid is not allowed.
6. The answer key and worked solutions are at the end of this booklet. Attempt the paper in 60 minutes before you look at them.

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**Topics covered:** Classification and structure · Preparation of amines · Basicity of amines · Chemical reactions of amines · Identification of amines · Diazonium salts

## SECTION A (Q1–20) · Multiple choice · +4 / 0 / −1

Each question has FOUR options. ONLY ONE of them is correct.

**1.** Which of the following is a suitable method for preparing 2-methylpropan-2-amine, $(CH_3)_3C–NH_2$?

(1) Gabriel phthalimide synthesis using 2-bromo-2-methylpropane

(2) heating 2-bromo-2-methylpropane with excess ammonia

(3) Hoffmann bromamide degradation of 2,2-dimethylpropanamide, $(CH_3)_3C–CONH_2$

(4) reduction of 2-methylpropanenitrile, $(CH_3)_2CH–CN$, with $LiAlH_4$

**2.** The correct order of basic strength of the following is

(1) $C_6H_5NH_2$ > $C_6H_5CH_2NH_2$ > 4-methoxyaniline > 4-nitroaniline

(2) $C_6H_5CH_2NH_2$ > 4-methoxyaniline > $C_6H_5NH_2$ > 4-nitroaniline

(3) 4-methoxyaniline > $C_6H_5CH_2NH_2$ > $C_6H_5NH_2$ > 4-nitroaniline

(4) $C_6H_5CH_2NH_2$ > $C_6H_5NH_2$ > 4-nitroaniline > 4-methoxyaniline

**3.** An amine $C_3H_9N$ reacts with benzenesulphonyl chloride to give a solid that is insoluble in aqueous KOH. The amine is

(1) propan-1-amine

(2) propan-2-amine

(3) N-methylethanamine

(4) N,N-dimethylmethanamine

**4.** Benzenediazonium chloride reacts with aniline in a mildly acidic medium. The product is

(1) 4-aminoazobenzene (aniline yellow)

(2) 4-hydroxyazobenzene

(3) diphenylamine

(4) biphenyl

**5.** Benzenediazonium chloride is treated with fluoroboric acid, and the precipitate formed is heated with aqueous $NaNO_2$ in the presence of copper. The product is

(1) fluorobenzene

(2) nitrobenzene

(3) phenol

(4) benzene

**6.** Nitrobenzene is reduced to aniline on an industrial scale with scrap iron and hydrochloric acid, and only a small amount of the acid is needed. This is because

(1) iron is a catalyst and is not used up

(2) aniline formed reacts with HCl to give more acid

(3) hydrogen gas from the air also reduces nitrobenzene

(4) the $FeCl_2$ formed is hydrolysed and releases HCl again

**7.** Methyl isocyanide, $CH_3–N{\equiv}C$, is reduced with $LiAlH_4$ (or $H_2$/Ni). The product is

(1) ethanamine

(2) N-methylmethanamine

(3) methanamine

(4) N,N-dimethylmethanamine

**8.** Which of the following amines gives a yellow oily N-nitroso compound with $NaNO_2$ and HCl at 273 K?

(1) N,N-dimethylmethanamine

(2) ethanamine

(3) propan-2-amine

(4) N-ethylethanamine

**9.** In the gas phase, where there is no solvation, the correct order of basic strength is

(1) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$

(2) $NH_3 > CH_3NH_2 > (CH_3)_2NH > (CH_3)_3N$

(3) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

(4) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

**10.** Benzylamine, $C_6H_5CH_2NH_2$, is treated with $NaNO_2$ and HCl at 273 K. The main organic product is

(1) a stable benzyldiazonium chloride

(2) benzyl alcohol, with $N_2$ given off

(3) an N-nitrosamine

(4) 4-aminobenzyl chloride

**11.** N-Methylethanamide, $CH_3CONHCH_3$, is reduced with $LiAlH_4$ and the product is treated with water. The product is

(1) ethanamine and methanol

(2) N,N-dimethylmethanamine

(3) propan-1-amine

(4) N-methylethanamine

**12.** Aniline is treated with (i) bromine water, (ii) $NaNO_2$ and HCl at 273 K, and (iii) $H_3PO_2$. The final product is

(1) 1,3,5-tribromobenzene

(2) 1,2,4-tribromobenzene

(3) bromobenzene

(4) 2,4,6-tribromophenol

**13.** Acetanilide (N-phenylethanamide) is treated with bromine in ethanoic acid. The main product is

(1) 2,4,6-tribromoacetanilide

(2) 3-bromoacetanilide

(3) 4-bromoacetanilide

(4) 4-bromoaniline

**14.** Assertion A: N,N-Dimethylaniline does not react with benzenesulphonyl chloride.
Reason R: There is no hydrogen atom on the nitrogen of N,N-dimethylaniline that can be replaced by the $C_6H_5SO_2$ group.
In the light of the above statements, choose the correct answer from the options given below:

(1) Both A and R are true and R is the correct explanation of A

(2) Both A and R are true but R is NOT the correct explanation of A

(3) A is true but R is false

(4) A is false but R is true

**15.** Statement I: 4-Nitroaniline is a weaker base than 3-nitroaniline.
Statement II: A nitro group at the meta position cannot withdraw the lone pair of the amino nitrogen by resonance; it acts only by its −I effect.
In the light of the above statements, choose the correct answer from the options given below:

(1) Both Statement I and Statement II are true

(2) Statement I is true but Statement II is false

(3) Statement I is false but Statement II is true

(4) Both Statement I and Statement II are false

**16.** Aniline is converted into benzoic acid by the sequence

(1) $NaNO_2$/HCl at 273 K; CuCN/KCN; then $H_3O^+$, heat

(2) $NaNO_2$/HCl at 273 K; $H_2O$, warm; then $KMnO_4$

(3) $CH_3COCl$; then $KMnO_4$, heat

(4) $Br_2$ water; then Mg, $CO_2$, $H_3O^+$

**17.** Aniline is shaken with benzoyl chloride in the presence of aqueous NaOH. The product is

(1) benzophenone

(2) 4-aminobenzophenone

(3) N-phenylbenzamide (benzanilide)

(4) phenyl benzoate

**18.** Which of the following is the weakest base?

(1) ethanamine

(2) ammonia

(3) ethanamide

(4) aniline

**19.** Which isomer of $C_7H_9N$ forms a diazonium salt that is stable at 273–278 K when treated with $NaNO_2$ and HCl?

(1) benzylamine

(2) N-methylaniline

(3) 4-methylaniline

(4) none of the isomers

**20.** The hybridisation of nitrogen and the shape around it in trimethylamine are

(1) $sp^2$, trigonal planar

(2) $sp^3$, tetrahedral with all four positions occupied by atoms

(3) sp, linear

(4) $sp^3$, pyramidal (one position held by the lone pair)

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**SECTION B (Q21–25) · Numerical value · +4 / 0 / −1**

The answer to each question is a NUMERICAL VALUE. Enter it rounded off to the nearest integer.

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**21.** The total number of structurally isomeric amines with the molecular formula $C_4H_{11}N$ is _____.

Answer: _____

**22.** 24.6 g of nitrobenzene is reduced with Sn and HCl and the product is made alkaline. If the yield is 75%, the mass of aniline obtained (in g, to the nearest integer) is _____. (H = 1, C = 12, N = 14, O = 16)

Answer: _____

**23.** 0.59 g of a primary aliphatic amine reacts with nitrous acid to give 224 mL of nitrogen at STP. The molar mass of the amine (in g/mol) is _____. (Molar volume 22.4 L)

Answer: _____

**24.** The number of the following that are stronger bases than ammonia in aqueous solution is _____.
methylamine, dimethylamine, trimethylamine, aniline, N-methylaniline, ethanamide, 4-nitroaniline, ethylamine, diethylamine

Answer: _____

**25.** A 0.10 M aqueous solution of an amine has pH 11.3 at 298 K. Its Kb is $x \times 10^{-5}$. The value of x (to the nearest integer) is _____. ($K_w = 1.0 \times 10^{-14}$)

Answer: _____

**END OF THE QUESTION PAPER**

## ANSWER KEY

| Q1 | Q2 | Q3 | Q4 | Q5 | Q6 | Q7 | Q8 | Q9 | Q10 |
|---|---|---|---|---|---|---|---|---|---|
| (3) | (2) | (3) | (1) | (2) | (4) | (2) | (4) | (3) | (2) |

| Q11 | Q12 | Q13 | Q14 | Q15 | Q16 | Q17 | Q18 | Q19 | Q20 |
|---|---|---|---|---|---|---|---|---|---|
| (4) | (1) | (3) | (1) | (1) | (1) | (3) | (3) | (3) | (4) |

| Q21 | Q22 | Q23 | Q24 | Q25 |
|---|---|---|---|---|
| 8 | 14 | 59 | 5 | 4 |

## WORKED SOLUTIONS

**Q1. Answer (3).** In the Hoffmann degradation the alkyl group moves from the carbonyl carbon to nitrogen with its structure unchanged: $(CH_3)_3C–CONH_2 + Br_2 + 4NaOH \rightarrow (CH_3)_3C–NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$. A tertiary halide gives mainly 2-methylpropene with phthalimide ion or ammonia (elimination, as SN2 is blocked), and the nitrile gives $(CH_3)_2CHCH_2NH_2$, 2-methylpropan-1-amine.

**Q2. Answer (2).** In benzylamine the $–NH_2$ is on an $sp^3$ carbon, so its lone pair is not delocalised into the ring (pKb 4.70). In the anilines it is, so they are much weaker; a para $–OCH_3$ pushes electron density back (pKb 8.66), and a para $–NO_2$ withdraws it strongly (pKb 13.0). Aniline is 9.38.

**Q3. Answer (3).** Hinsberg test: a primary amine gives a sulphonamide $C_6H_5SO_2NHR$ whose N–H is acidic, so it dissolves in alkali; a secondary amine gives $C_6H_5SO_2NR_2$, which has no H on N and is insoluble in alkali; a tertiary amine does not react. The secondary amine of formula $C_3H_9N$ is $CH_3NHCH_2CH_3$.

**Q4. Answer (1).** The diazonium ion is a weak electrophile and attacks the strongly activated para position of aniline (coupling): $C_6H_5N_2^+ + C_6H_5NH_2 \rightarrow C_6H_5–N=N–C_6H_4–NH_2$ (para) $+ H^+$. The product is the yellow dye 4-aminoazobenzene.

**Q5. Answer (2).** $HBF_4$ precipitates the diazonium fluoroborate $C_6H_5N_2^+BF_4^-$. Heating this with $NaNO_2$ and copper replaces the diazonium group by $–NO_2$: $C_6H_5N_2^+BF_4^- + NaNO_2 \rightarrow C_6H_5NO_2 + N_2 + NaBF_4$. (Heating the dry fluoroborate alone would give fluorobenzene.)

**Q6. Answer (4).** $Fe + 2HCl \rightarrow FeCl_2 + H_2$ supplies the reducing agent; the $FeCl_2$ formed is hydrolysed by water, releasing HCl, so the acid is regenerated and only a little is needed to start the reaction.

**Q7. Answer (2).** Reduction of an isocyanide adds hydrogen to the isocyanide carbon, which stays attached to nitrogen: $CH_3–N≡C + 4[H] \rightarrow CH_3–NH–CH_3$, a secondary amine. (The isomeric nitrile $CH_3–C≡N$ gives the primary amine ethanamine.)

**Q8. Answer (4).** Secondary amines, $R_2NH$, react with nitrous acid to give N-nitrosamines, $R_2N–N=O$, yellow oils. Primary aliphatic amines give an alcohol and $N_2$ through an unstable diazonium ion, and tertiary aliphatic amines only form a salt.

**Q9. Answer (3).** Without solvent, only the electron-releasing (+I) effect of the alkyl groups matters, and each extra methyl group makes the lone pair more available: tertiary > secondary > primary > $NH_3$. In water the order changes because of solvation.

**Q10. Answer (2).** Benzylamine is a primary aliphatic amine ($–NH_2$ on an $sp^3$ carbon), not an aromatic amine. Its diazonium ion is not stabilised by the ring and loses $N_2$ at once, even at 273 K; the carbocation reacts with water to give $C_6H_5CH_2OH$.

**Q11. Answer (4).** $LiAlH_4$ reduces the C=O of an amide to $CH_2$ without breaking the C–N bond: $CH_3CONHCH_3 \rightarrow CH_3CH_2NHCH_3$, N-methylethanamine (a secondary amine).

**Q12. Answer (1).** (i) The strongly activating $–NH_2$ directs Br to both ortho and the para positions: 2,4,6-tribromoaniline. (ii) Diazotisation gives the diazonium salt. (iii) $H_3PO_2$ replaces $–N_2^+$ by H. The three Br atoms are left alternate to each other:

1,3,5-tribromobenzene, a substitution pattern that cannot be made by brominating benzene directly.

**Q13. Answer (3).** The $–NHCOCH_3$ group is much less activating than $–NH_2$, because the nitrogen lone pair is also delocalised on to the C=O; so only one Br enters, and the bulky group favours the para position. Hydrolysis afterwards would give 4-bromoaniline, but it is not part of this step.

**Q14. Answer (1).** Sulphonylation replaces an N–H hydrogen by $C_6H_5SO_2–$. A tertiary amine (aromatic or not) has no N–H, so it does not react. Both true; R explains A.

**Q15. Answer (1).** A para $–NO_2$ group pulls the nitrogen lone pair into the ring and on to its own oxygens by resonance (−R) as well as by −I, so 4-nitroaniline (pKb 13.0) is weaker than 3-nitroaniline (pKb 11.5), where only −I acts. Both statements are true.

**Q16. Answer (1).** Diazotisation gives $C_6H_5N_2^+Cl^-$; the Sandmeyer reaction with CuCN replaces $–N_2^+$ by –CN (benzonitrile); acid hydrolysis turns –CN into –COOH. Route 2 gives phenol, which $KMnO_4$ cannot turn into benzoic acid; route 4 starts with tribromination.

**Q17. Answer (3).** Benzoylation (Schotten–Baumann reaction): the amino group attacks the acyl chloride, replacing a hydrogen on nitrogen by $C_6H_5CO–$: $C_6H_5NH_2 + C_6H_5COCl \rightarrow C_6H_5NHCOC_6H_5 + HCl$, and NaOH removes the HCl.

**Q18. Answer (3).** In an amide the nitrogen lone pair is delocalised on to the C=O group, which is strongly electron-withdrawing, so ethanamide is almost neutral (pKb about 14.5). Aniline (9.38) is weaker than ammonia (4.75), and ethanamine (3.29) is the strongest.

**Q19. Answer (3).** Only primary aromatic amines ($–NH_2$ directly on a benzene ring) give diazonium salts that are stable in cold solution, because the positive charge is delocalised into the ring. 4-Methylaniline is one. Benzylamine is a primary aliphatic amine and N-methylaniline is secondary.

**Q20. Answer (4).** Nitrogen has three bond pairs and one lone pair: four electron pairs, $sp^3$. With the lone pair in one position the C–N–C framework is pyramidal (angle about 108°).

**Q21. Answer 8.** Primary (4): butan-1-amine, butan-2-amine, 2-methylpropan-1-amine, 2-methylpropan-2-amine. Secondary (3): N-methylpropan-1-amine, N-methylpropan-2-amine, N-ethylethanamine. Tertiary (1): N,N-dimethylethanamine. Total 8.

**Q22. Answer 14.** $C_6H_5NO_2$ (123 g/mol): 24.6/123 = 0.20 mol → 0.20 mol $C_6H_5NH_2$ in theory. At 75%: 0.15 mol × 93 g/mol = 13.95 g, i.e. 14.

**Q23. Answer 59.** $RNH_2 + HNO_2 \rightarrow ROH + N_2 + H_2O$: one mole of $N_2$ per mole of amine. $N_2$ = 0.224/22.4 = 0.010 mol, so M = 0.59/0.010 = 59 g/mol ($C_3H_7NH_2$).

**Q24. Answer 5.** pKb of $NH_3$ = 4.75. Lower pKb (stronger base): methylamine 3.38, dimethylamine 3.27, trimethylamine 4.22, ethylamine 3.29 and diethylamine 3.00: 5. Aniline (9.38), N-methylaniline (9.30), 4-nitroaniline (13.0) and ethanamide (about 14.5) are weaker.

**Q25. Answer 4.** pOH = 14 − 11.3 = 2.7, so $[OH^-] = 10^{-2.7} = 2.0 \times 10^{-3}$ M. $K_b = (2.0 \times 10^{-3})^2/(0.10 − 0.0020) = 4.0 \times 10^{-6}/0.098 = 4.1 \times 10^{-5}$. x = 4.

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