Class 12 Chemistry · Chapter 9: Amines

Answer key and marking scheme · 20 marks · about 40 minutes · based on NCERT

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1. Which of these amines can be prepared by the Gabriel phthalimide synthesis? [1]

(a) 2-phenylethanamine (b) N-methylpropan-1-amine

(c) 4-methylaniline (d) N,N-dimethylethanamine

Answer: (a) Gabriel synthesis gives only primary amines, from alkyl halides: (2-bromoethyl)benzene, $C_6H_5CH_2CH_2Br$, gives $C_6H_5CH_2CH_2NH_2$. 4-Methylaniline would need an aryl halide, which does not substitute with the phthalimide anion; (b) and (d) are secondary and tertiary.

2. Which of the following isomers of $C_5H_{13}N$ has the highest boiling point? [1]

(a) N,N-dimethylpropan-1-amine (b) N-methylbutan-1-amine

(c) pentan-1-amine (d) N-ethyl-N-methylethanamine

Answer: (c) Primary amines have two N–H hydrogens for hydrogen bonding and associate most; secondary amines have one; tertiary amines, (a) and (d), have none. So the boiling point order of isomers is 1° > 2° > 3°.

3. Pentanamide, $CH_3(CH_2)_3CONH_2$, is warmed with bromine and aqueous sodium hydroxide. The organic product is [1]

(a) butan-1-amine (b) pentan-1-amine

(c) butanenitrile (d) sodium pentanoate

Answer: (a) In Hoffmann bromamide degradation the alkyl group migrates from the carbonyl carbon to nitrogen and the carbonyl carbon leaves as Na_2CO_3: the amine, $CH_3(CH_2)_3NH_2$, has one carbon less than the amide.

4. An aromatic amine C_7H_9N has $-NH_2$ and $-CH_3$ on the benzene ring, para to each other. Its IUPAC name is [1]

(a) phenylmethanamine (b) 2-methylaniline

(c) N-methylaniline (d) 4-methylaniline

Answer: (d) Both groups are on the ring, so the parent is aniline, with $-CH_3$ at C-4. 2-Methylaniline is the ortho isomer; N-methylaniline has CH_3 on nitrogen; phenylmethanamine, $C_6H_5CH_2NH_2$, has $-NH_2$ off the ring.

5. The IUPAC name of $CH_3CH_2CH_2–NH–CH_2CH_3$ is [1]

(a) N-propylethanamine (b) N-ethylpropan-2-amine

(c) ethylpropylamine (d) N-ethylpropan-1-amine

Answer: (d) The longer chain on nitrogen, propyl, gives the parent propan-1-amine; the ethyl group on nitrogen takes the locant N. Ethylpropylamine is the common name, not the IUPAC name; (a) takes the shorter chain as parent; (b) puts the nitrogen on C-2.

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6. (a) Draw the structure of N-ethyl-N-methylpropan-1-amine and classify it as primary, secondary or tertiary. (b) A primary amine isomeric with it has an unbranched six-carbon chain with the $-NH_2$ group on the third carbon. Write its structure and IUPAC name. [2]

(a) $CH_3CH_2CH_2-N(CH_3)-CH_2CH_3$: propyl is the longest chain, and the ethyl and methyl groups carry the locant N. All three hydrogens of NH_3 are replaced, so it is a tertiary amine ($C_6H_{15}N$). (b) $CH_3CH_2CH(NH_2)CH_2CH_2CH_3$, also $C_6H_{15}N$: the 'e' of hexane is replaced by 'amine' with the locant of the carbon bearing $-NH_2$, hexan-3-amine; one hydrogen of NH_3 replaced, so primary.

- (a) correct structure, tertiary (1)
- (b) $CH_3CH_2CH(NH_2)CH_2CH_2CH_3$, hexan-3-amine (1)

7. The $-NHCOCH_3$ group of acetanilide activates the benzene ring less than the $-NH_2$ group of aniline. Explain, showing the resonance involved. [2]

In acetanilide the lone pair on nitrogen is in resonance with the carbonyl oxygen: $>N-C(=O)-CH_3 \leftrightarrow >N^+=C(-O^-)-CH_3$. Part of the lone pair is thus drawn towards oxygen and is less available for donation to the ring, so $-NHCOCH_3$ is a milder activator than $-NH_2$.

- resonance $>N-C(=O)CH_3 \leftrightarrow >N^+=C(O^-)CH_3$ shown (1)
- lone pair less available to the ring, so less activation (1)

8. Using the stability of the cation formed, explain why ethanamine is a stronger base than ammonia. [2]

$C_2H_5NH_2 + H^+ \rightleftharpoons C_2H_5NH_3^+$ and $NH_3 + H^+ \rightleftharpoons NH_4^+$. The ethyl group pushes electrons towards nitrogen (+I effect), so its unshared pair is more available to a proton; and the same +I effect disperses the positive charge of $C_2H_5NH_3^+$, making it more stable relative to the amine than NH_4^+ is relative to NH_3. The more stable the cation, the more basic the amine.

- +I effect makes the lone pair more available (1)
- the ethylammonium ion is stabilised by charge dispersal, so the amine is more basic (1)

9. Starting from 1-bromopropane: (a) write equations to prepare propan-1-amine free of secondary and tertiary amines; (b) state what heating 1-bromopropane with ethanolic ammonia in a sealed tube would give, and why. (c) To make the reaction in (b) go faster, would you replace 1-bromopropane by 1-chloropropane or by 1-iodopropane? Give the order of reactivity on which you decide. [3]

(a) Gabriel synthesis: phthalimide + ethanolic KOH → potassium phthalimide; with $CH_3CH_2CH_2Br$ on heating → N-propylphthalimide; hydrolysis with NaOH(aq) → $CH_3CH_2CH_2NH_2$ + the disodium salt of phthalic acid. Only a primary amine can form. (b) A mixture of propan-1-amine, N-propylpropan-1-amine, tripropylamine and the quaternary salt $(CH_3CH_2CH_2)_4N^+Br^-$, because each amine formed is itself a nucleophile and reacts further with the halide. (c) 1-Iodopropane: the reactivity of halides with amines is RI > RBr > RCl, so the iodide reacts faster and the chloride slower.

- (a) Gabriel route with the three stages (1)
- (b) mixture of 1°, 2°, 3° amines and quaternary salt, with reason (1)
- (c) 1-iodopropane, RI > RBr > RCl (1)

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10. In water, trimethylamine is a weaker base than methanamine, but triethylamine is a stronger base than ethanamine. Show how the inductive effect, solvation and steric hindrance bear on this, and write the order of basic strength in water of the three ethylamines and ammonia. [3]

1. The +I effect of alkyl groups raises the electron density on nitrogen and stabilises the cation; on this alone basicity would be 3° > 2° > 1°, the order seen in the gas phase. 2. In water the cations are also stabilised by hydrogen bonding with water: RNH_3^+ has three N–H, $R_2NH_2^+$ two, R_3NH^+ one, so on solvation alone the order would be 1° > 2° > 3°. 3. A methyl group causes no steric hindrance to hydrogen bonding, so the poorer solvation of $(CH_3)_3NH^+$ puts $(CH_3)_3N$ below CH_3NH_2. The bigger ethyl group does hinder hydrogen bonding, and this changes the balance of the three factors: the observed order in water is $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$.

- inductive effect alone favours 3° > 2° > 1° (1)
- solvation by H-bonding favours 1° > 2° > 3°; CH_3 gives no steric hindrance, so $(CH_3)_3NH^+$ least solvated and $(CH_3)_3N < CH_3NH_2$ (1)
- C_2H_5 hinders H-bonding, changing the balance; order $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ (1)

11. How would you obtain each of the following from 4-chloroaniline? Give reagents and conditions. (a) 1,4-dichlorobenzene (b) 4-chlorophenol (c) chlorobenzene [3]

First diazotise: $Cl–C_6H_4–NH_2 + NaNO_2 + 2HCl \rightarrow Cl–C_6H_4–N_2^+Cl^- + NaCl + 2H_2O$, at 273–278 K. (a) Sandmeyer: with Cu_2Cl_2/HCl → $Cl–C_6H_4–Cl + N_2$. (b) Let the solution warm to 283 K: the salt is hydrolysed, $Cl–C_6H_4–OH + N_2 + HCl$. (c) Hypophosphorous acid and water (or ethanol): $Cl–C_6H_4–N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow C_6H_5Cl + N_2 + H_3PO_3 + HCl$.

- diazotisation in the cold, then Cu_2Cl_2/HCl for (a) (1)
- (b) warming to 283 K, hydrolysis to the phenol (1)
- (c) H_3PO_2 and water (or ethanol) replaces the diazo group by H (1)

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