Unit 16 · Amines

ANSWER KEY · FOR TEACHERS

Full marks 36

Give the marks for the points in the marking scheme; an answer in other words that says the same is right.

1 Key words

1. chloroform and alcoholic KOH → **d.** a foul-smelling isocyanide from a primary amine only
2. cold $NaNO_2$ and dilute HCl with a secondary amine → **e.** a yellow oily N-nitrosamine
3. diethyl oxalate → **f.** separates 1°, 2° and 3° amines
4. Br_2 and aqueous KOH with an amide → **g.** a primary amine with one carbon fewer
5. $LiAlH_4$ with an amide → **c.** a primary amine with the same number of carbons
6. $NaNO_2$ and HCl with aniline at 0–5 °C → **a.** benzenediazonium chloride

K · 3

Each carries 0.5 mark.

2 Label the diagram

1. Solid: dialkyloxamide
2. Filtrate: oxamic ester and 3° amine
3. 2° amine
4. Distills first: 3° amine

U · 2

Each carries 0.5 mark.

3 Multiple choice

i. **b.** secondary amine — K · 1

Amines are classed by the number of carbon groups on the nitrogen: here two, an ethyl and a methyl.

ii. **b.** 1° amine > 2° amine > 3° amine — U · 1

A primary amine has two N–H hydrogens to hydrogen-bond with, a secondary one and a tertiary none: propan-1-amine 48 °C, N-methylethanamine 37 °C, N,N-dimethylmethanamine 3 °C.

iii. **c.** aniline — U · 1

Aniline's lone pair is delocalized into the ring, so it is far less available to take a proton.

iv. **c.** a white precipitate of 2,4,6-tribromoaniline — A · 1

The $-NH_2$ group activates the ring so strongly that all three ortho and para places are brominated, with no catalyst.

v. **b.** an orange dye, 4-hydroxyazobenzene — K · 1

The diazonium ion attacks phenol's para carbon and joins it by an –N=N– group: 4-hydroxyazobenzene, orange.

4 Short answers

a. MARKING SCHEME — A · 2

- ✓ $C_2H_5Br + 2\,NH_3 \xrightarrow{\text{ethanol, heat, sealed tube}} C_2H_5NH_2 + NH_4Br$ (a large excess of ammonia).
- ✓ $CH_3CN + 4\,[H] \xrightarrow{Na,\ \text{ethanol}} CH_3CH_2NH_2$

b. MARKING SCHEME — U · 2

- ✓ The amine formed has a lone pair and is a better nucleophile than ammonia, so it attacks the haloalkane too, giving 2° and 3° amines and a quaternary salt.
- ✓ A large excess of ammonia makes each haloalkane molecule far more likely to meet ammonia, so the primary amine is the main product.

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c. MARKING SCHEME U · 2

- ✓ Ethanamine gives brisk bubbles of nitrogen: $C_2H_5NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2\uparrow + H_2O$
- ✓ N-Ethylethanamine gives a yellow oily N-nitrosamine: $(C_2H_5)_2NH + HNO_2 \rightarrow (C_2H_5)_2N{-}NO + H_2O$

d. MARKING SCHEME U · 2

- ✓ Aniline's nitrogen lone pair overlaps with the ring's π electrons and is partly delocalized, so it is less available to take a proton.
- ✓ The ion $C_6H_5NH_3^+$ has no lone pair left to delocalize, so protonation would destroy aniline's extra resonance stability (the ring also pulls electrons slightly, −I).

e. MARKING SCHEME A · 3

- ✓ The balanced equation.
- ✓ A use: an early fever medicine (Antifebrin).
- ✓ Acetylation tones down the $-NH_2$ group so substitution can be controlled.

5 Long answer

ANSWER A · 4

i. With sodium nitrite and dilute HCl at 0–5 °C:
$C_6H_5NH_2 + NaNO_2 + 2\,HCl \xrightarrow{0\text{–}5\ ^\circ C} C_6H_5N_2{+}Cl^- + NaCl + 2\,H_2O$

ii. Benzenediazonium chloride coupled with aniline in faintly acidic solution at 0–5 °C:
$C_6H_5N_2{+}Cl^- + C_6H_5NH_2 \xrightarrow{0\text{–}5\ ^\circ C} C_6H_5N{=}N{-}C_6H_4NH_2 + HCl$, a yellow dye.

iii. Warmed with chloroform and alcoholic KOH:
$C_6H_5NH_2 + CHCl_3 + 3\,KOH \rightarrow C_6H_5NC + 3\,KCl + 3\,H_2O$

iv. With bromomethane: $C_6H_5NH_2 + CH_3Br \rightarrow C_6H_5NHCH_3 + HBr$

MARKING SCHEME

- ✓ Diazotization, with 0–5 °C and the equation.
- ✓ Coupling with aniline and the equation.
- ✓ Carbylamine reaction and the equation.
- ✓ Alkylation with bromomethane and the equation.

6 Numerical problems

a. ANSWER A · 4

i. $CH_3CH_2CONH_2 + Br_2 + 4\,KOH \rightarrow CH_3CH_2NH_2 + K_2CO_3 + 2\,KBr + 2\,H_2O$: **ethanamine**, one carbon fewer.

ii. Propanamide, $C_3H_7NO = 36 + 7 + 14 + 16 = 73$ g/mol: 7.30 g ÷ 73 = 0.100 mol. Ethanamine, $C_2H_7N = 45$ g/mol: $0.100 \times 45 \times 0.80 =$ **3.60 g**.

iii. Br_2: 0.100 mol × 160 g/mol = **16.0 g**; KOH: 0.400 mol × 56 g/mol = **22.4 g**.

MARKING SCHEME

- ✓ The balanced equation, ethanamine.
- ✓ 0.100 mol of amide.
- ✓ 3.60 g of ethanamine.
- ✓ 16.0 g of Br_2 and 22.4 g of KOH.

b. ANSWER A · 4

i. Methanamine Kb = $10^{-3.34} =$ **4.6×10^{-4}**; aniline Kb = $10^{-9.13} =$ **7.4×10^{-10}**.

ii. 10^(9.13 − 3.34) = $10^{5.79} \approx$ **6.2×10^5 times**.

iii. Methanamine: $[OH^-] = \sqrt{(4.6 \times 10^{-4} \times 0.10)} = 6.8 \times 10^{-3}$ M, pOH = 2.17, **pH = 11.83**. Aniline: $[OH^-] = \sqrt{(7.4 \times 10^{-10} \times 0.10)} = 8.6 \times 10^{-6}$ M, pOH = 5.07, **pH = 8.93**.

iv. Both are bases, but aniline gives a solution only slightly alkaline: its lone pair, delocalized into the ring, takes protons from water far less readily.

MARKING SCHEME

- ✓ Both Kb values.
- ✓ About 6.2×10^5 times.
- ✓ pH 11.83 and 8.93.
- ✓ Aniline is a far weaker base, because its lone pair is delocalized.

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7 Think

ANSWER HA · 3

Alkyl groups push electrons onto the nitrogen (+I), so with no solvent each extra alkyl group makes the amine a stronger base, and the tertiary amine is strongest. In water, the ion formed is also stabilized by hydrogen bonds to water through its N–H hydrogens: R_3NH^+ has only one, $R_2NH_2^+$ two, RNH_3^+ three. The tertiary amine's ion is the least hydrated, and its three groups crowd the nitrogen, so in water it falls behind the secondary and primary amines.

MARKING SCHEME

- ✓ The +I effect alone gives 3° > 2° > 1° in the gas.
- ✓ In water the protonated amine is stabilized by hydrogen bonding through its N–H hydrogens, fewest for R_3NH^+.
- ✓ Less hydration and more crowding put the 3° amine below the 2° and 1°.

8 Activity: Three bottles

(not marked)

WHAT STUDENTS SHOULD FIND

Ethanamine (1°): brisk bubbles of colorless nitrogen; ethanol. N-Ethylethanamine (2°): a yellow oily layer; N-nitrosodiethylamine. N,N-Diethylethanamine (3°): a clear solution, no change; a soluble triethylammonium nitrite. The carbylamine test (chloroform and alcoholic KOH) confirms the primary amine; it is done only in a fume cupboard because the isocyanide is toxic and foul-smelling and chloroform is harmful (and N-nitrosamines cause cancer in laboratory animals).

Marks by level	Knowledge	Understanding	Application	Higher ability	Total
Marks	5	10	18	3	**36**

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