Week 51

A-Level Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

Contents 目录

A-Level Chemistry Name: _____ Score: _____

1. A primary amine has the group:
   - ☐ $–NH_2$
   - ☐ –COOH
   - ☐ –OH
   - ☐ –COO–
2. Phenylamine is made from benzene by:
   - ☐ nitrating to nitrobenzene, then reducing (Sn/conc. HCl, then NaOH)
   - ☐ adding water
   - ☐ oxidising with $KMnO_4$
   - ☐ free-radical substitution
3. An amide is made from an acyl chloride and:
   - ☐ ammonia or a primary amine
   - ☐ an alcohol
   - ☐ water
   - ☐ an alkene
4. An amino acid contains:
   - ☐ both a basic $–NH_2$ group and an acidic –COOH group
   - ☐ only an $–NH_2$ group
   - ☐ only a –COOH group
   - ☐ a C=C double bond
5. A primary amine is made by heating a halogenoalkane with:
   - ☐ ammonia in ethanol, under pressure
   - ☐ water
   - ☐ acidified dichromate
   - ☐ bromine
6. Amines act as bases because the nitrogen has a lone _____.

7. Phenylamine can be used to make azo dyes via a diazonium salt.

   ☐ True ☐ False

8. The functional group –$CONH_2$ is found in an _____.

   _____

9. Amino acids contain both an amino group and a carboxylic acid group.

   ☐ True ☐ False

10. The order of basicity is:

    ☐ phenylamine < ammonia < ethylamine

    ☐ ethylamine < ammonia < phenylamine

    ☐ all equal

    ☐ ammonia < ethylamine < phenylamine

34. Nitrogen compounds

Answers · 答案

A-Level Chemistry

1. **–NH_2**

   A primary amine has –NH_2; a secondary amine has –NH– between two carbons.

2. **nitrating to nitrobenzene, then reducing (Sn/conc. HCl, then NaOH)**

   Benzene → nitrobenzene (nitration) → phenylamine (reduction with tin and acid, then NaOH).

3. **ammonia or a primary amine**

   Ammonia or a 1°/2° amine reacts with an acyl chloride to give an amide.

4. **both a basic –NH_2 group and an acidic –COOH group**

   Having both groups is what makes amino acids behave as they do (zwitterions, peptide bonds).

5. **ammonia in ethanol, under pressure**

   Ammonia substitutes the halogen to give the amine (excess NH_3 favours the primary amine).

6. **pair**

   It accepts a proton.

7. **True**

   Azo compounds are brightly coloured.

8. **amide**

   Formed from an acyl chloride and ammonia or an amine.

9. **True**

   They can act as both acid and base (zwitterions).

10. **phenylamine < ammonia < ethylamine**

    Ethylamine's alkyl group makes its lone pair most available; phenylamine's lone pair is delocalised into the ring, so it is weakest.

A-LEVEL CHEMISTRY • EXERCISE SHEET

34.1 Primary and secondary amines

Name: _____ Class: _____ Date: _____ **Total: 23 marks**

KEY WORDS amine 胺 • amide 酰胺 • basicity 碱性 • ammonia 氨 • reduction 还原

Objective

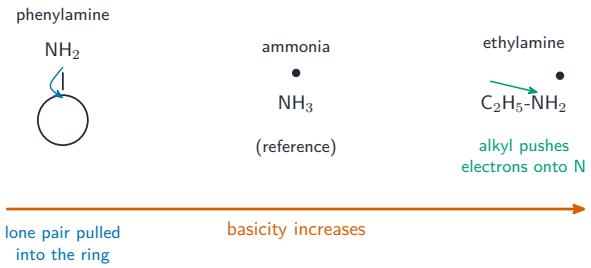
Build the skills to answer exam questions on **primary and secondary amines** 胺 — how they are made, and the trends in **basicity** 碱性.

You must be able to:

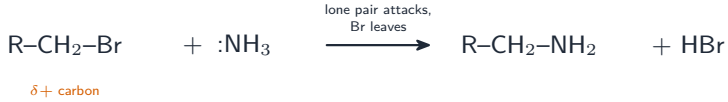
- give the reagents to make amines (from halogenoalkanes, amides, nitriles)
- explain why amines are basic
- explain and compare the basicity of ammonia, an aliphatic amine and phenylamine

1 Worked examples

Basicity



Basicity depends on the N lone pair: an alkyl group makes it more available (ethylamine strongest); a ring pulls it away (phenylamine weakest)



Routes to primary and secondary amines

- amines are basic because the **N lone pair** can accept an H^+.
- **basicity:** phenylamine < ammonia < ethylamine.
  - ethylamine: alkyl group pushes electrons onto N → lone pair more available → strongest.
  - phenylamine: lone pair delocalised into the ring → less available → weakest.
- **make a primary amine:** halogenoalkane + excess NH_3 in ethanol, heat under pressure; or reduce a nitrile/amide with $LiAlH_4$.

2 Practice

2.1 State why an amine is able to act as a base. [1]

2.2 Give the reagents to convert bromoethane into ethylamine. [2]

3 Exam-style questions

3.1 Which is the **strongest** base? [1]

- **A** phenylamine
- **B** ammonia
- **C** ethylamine
- **D** they are equal

3.2 Reduction of a nitrile, CH_3CN, with $LiAlH_4$ gives: [1]

- **A** ethylamine
- **B** ethanamide
- **C** ethanoic acid
- **D** ethanenitrile

3.3 Explain why ethylamine is a stronger base than ammonia. [2]

3.4 Explain why phenylamine is a much weaker base than ethylamine. [3]

3.5 Three bases are compared: ammonia, ethylamine and phenylamine.

(a) Place the three in order of increasing basicity and explain the order in terms of the availability of the nitrogen lone pair. [4]

(b) Ethylamine can be made from bromoethane and excess ethanolic ammonia. Write the equation, name the mechanism, and explain why an **excess** of ammonia is used. [4]

(c) Phenylamine is made from nitrobenzene. Give the reagents and conditions, and write the equation using [H] for the reducing agent. [3]

(d) Write the equation for ethylamine reacting with dilute hydrochloric acid, and name the salt. [2]

Solutions

2.1 the nitrogen lone pair can accept (donate to) an H^+.

2.2 excess ammonia, NH_3, in ethanol; heat under pressure.

3.1 C. Ethylamine — the alkyl group makes the lone pair most available.

3.2 A. $LiAlH_4$ reduces the nitrile to a primary amine, ethylamine.

3.3 the ethyl group pushes electron density onto the nitrogen (positive inductive effect); this makes the lone pair more available to accept an H^+, so ethylamine is a stronger base than ammonia.

3.4 in phenylamine the nitrogen lone pair overlaps with / is delocalised into the benzene ring; so it is less available to accept an H^+; whereas in ethylamine the lone pair is fully available (and the alkyl group pushes electrons onto N), so phenylamine is much weaker.

3.5 (a) phenylamine < ammonia < ethylamine. A base donates the nitrogen lone pair, so the more available that pair, the stronger the base. In ethylamine the ethyl group **releases** electron density inductively towards the nitrogen, making the lone pair more available; in phenylamine the lone pair is delocalised into the benzene ring, so it is much less available.
(b) $CH_3CH_2Br + 2NH_3 \rightarrow CH_3CH_2NH_2 + NH_4Br$; the mechanism is **nucleophilic substitution**; an excess of ammonia makes it more likely that ammonia — not the ethylamine already made — attacks the next bromoethane, which limits further substitution to secondary and tertiary amines.
(c) Tin and concentrated hydrochloric acid, heated under reflux, then made alkaline with sodium hydroxide; $C_6H_5NO_2 + 6[H] \rightarrow C_6H_5NH_2 + 2H_2O$.
(d) $CH_3CH_2NH_2 + HCl \rightarrow CH_3CH_2NH_3^+Cl^-$; **ethylammonium chloride**.

9 **(a)** Explain why amides are much weaker bases than amines.

.....

.....

.....

..... [2]

(b) Fig. 9.1 shows the preparation of 2-phenylethylamine, $C_6H_5CH_2CH_2NH_2$, by three different routes.

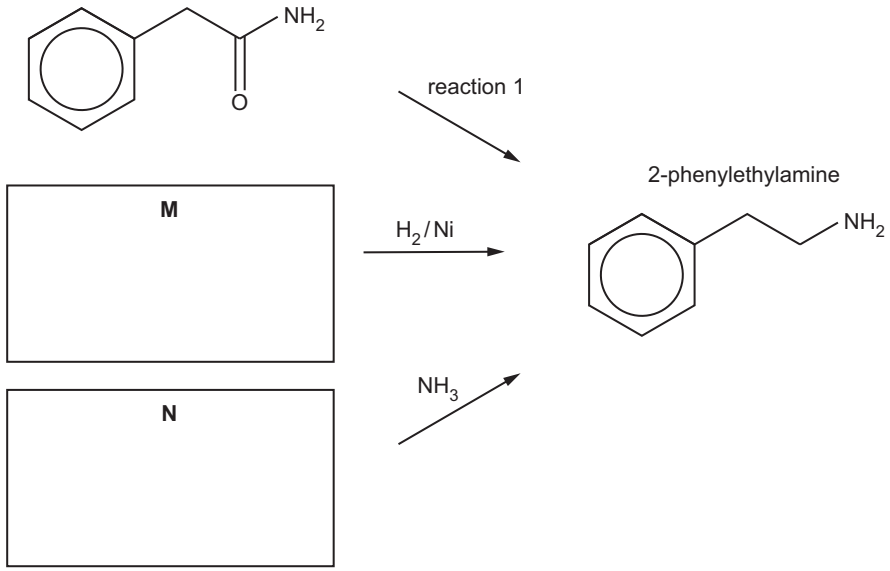


Fig. 9.1

(i) Suggest structures for compounds **M** and **N** and draw them in the boxes in Fig. 9.1. [2]

(ii) Give the reagents and conditions for reaction 1.

..... [1]

(c) Fig. 9.2 shows compound **H** which is a useful starting material in organic synthesis.

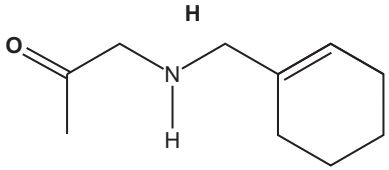


Fig. 9.2

H contains an alkene and an amine functional group.

Name the **other** functional group and give the classification of the amine group in **H**.

other functional group in **H** .....

classification of amine .....

[1]

(d) Ozonolysis involves the oxidative cleavage of a C=C bond in alkenes using ozone, O_3, as shown in Fig. 9.3.

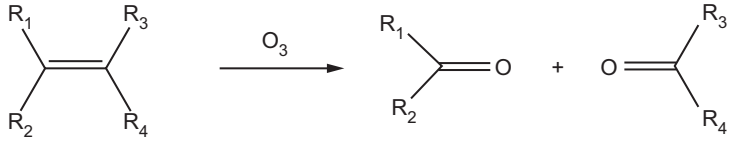


Fig. 9.3

Fig. 9.4 shows the first step in this reaction which involves the formation of an ozonide intermediate.

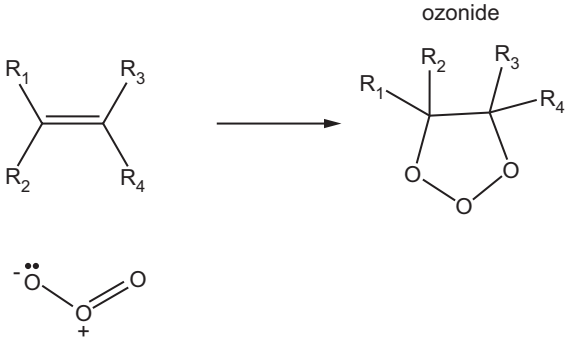
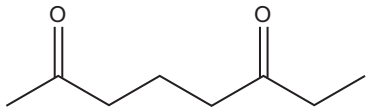


Fig. 9.4

(i) On Fig. 9.4, draw **three** curly arrows to complete the mechanism of this step. [2]

(ii) **L** is formed from alkene **K**, C_8H_{14}, by a similar reaction to that shown in Fig. 9.3.

L



Suggest the structure of **K**.

K C_8H_{14}

[1]

[Total: 9]

Important values, constants and standards

molar gas constant	$R = 8.31\,J\,K^{-1}\,mol^{-1}$
Faraday constant	$F = 9.65 \times 10^4\,C\,mol^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23}\,mol^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,C$
molar volume of gas	$V_m = 22.4\,dm^3\,mol^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,dm^3\,mol^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,kJ\,kg^{-1}\,K^{-1}$ ($4.18\,J\,g^{-1}\,K^{-1}$)

The Periodic Table of Elements

Group 1	2												13	14	15	16	17	18
																		2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0								1 H hydrogen 1.0				5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3												13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

Key

atomic number
atomic symbol
name
relative atomic mass

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

A-LEVEL CHEMISTRY • EXERCISE SHEET

34.2 Phenylamine and azo compounds

Name: _____ Class: _____ Date: _____ **Total: 32 marks**

KEY WORDS phenylamine 苯胺 • azo compound 偶氮化合物 • phenylamine and azo compounds 苯胺与偶氮化合物 • phenol 苯酚 • dye 染料

Objective

Build the skills to answer exam questions on **phenylamine and azo compounds** 苯胺与偶氮化合物 — making phenylamine, diazonium salts, and azo dye coupling.

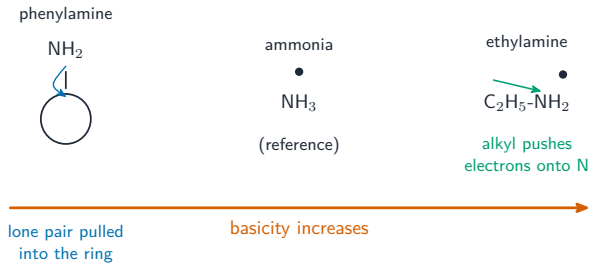
You must be able to:

- give the two-step route from benzene to phenylamine
- describe the formation of a diazonium salt and its conditions
- describe azo coupling and why azo compounds are coloured dyes

1 Worked examples

■ Diazonium salts and azo dyes

The strong colour of an azo dye comes from the –N=N– azo group joining two aromatic rings



Phenylamine is a weaker base than aliphatic amines

- **make phenylamine:** benzene → (nitrate) → nitrobenzene → (Sn / conc. HCl, then NaOH) → phenylamine.
- **diazonium salt:** phenylamine + $NaNO_2$ + dilute acid, **below 10 °C** → benzenediazonium chloride.
- **azo coupling:** diazonium salt + phenol in NaOH(aq) → a coloured **azo compound** (a dye); the –N=N– group links two rings.

■ Benzene to an azo dye, in three named steps

Step 1 — nitration. $C_6H_6 \rightarrow C_6H_5NO_2$ with concentrated HNO_3 and concentrated H_2SO_4 at 55 °C.

Step 2 — reduction to phenylamine 苯胺. $C_6H_5NO_2 \rightarrow C_6H_5NH_2$ with **tin and concentrated hydrochloric acid**, then **excess NaOH** to liberate the free amine from its salt. Both halves are marks; stopping at the tin/HCl step leaves you with the ammonium salt, not the amine.

Step 3 — diazotisation. $NaNO_2$ with dilute acid (which makes HNO_2 in situ) at **below 10 °C**, giving the **diazonium salt** 重氮盐 $C_6H_5N_2^+Cl^-$. The temperature is the mark: above about 10 °C the diazonium ion decomposes to phenol and nitrogen gas.

Step 4 — coupling. The diazonium salt is added to an alkaline solution of **phenol** (or another activated ring) to give an **azo compound** 偶氮化合物, an intensely coloured solid.

Why azo dyes are coloured. The two rings are joined through the $-N=N-$ **azo group**, which extends the **delocalised** system across the whole molecule. A larger delocalised system means a **smaller** energy gap between the levels, so the molecule absorbs light in the **visible** region, and the colour seen is the complement of what is absorbed. Changing the groups attached to the rings changes the gap, which is how a dye's colour is tuned.

Phenylamine is a weaker base than ethylamine — a favourite comparison. The nitrogen's lone pair is **delocalised into the benzene ring**, so it is less available to accept a proton. In ethylamine the alkyl group is electron-releasing and pushes

electron density onto the nitrogen, making the lone pair more available. Order: ethylamine > ammonia > phenylamine.

2 Practice

2.1 Give the reagents to reduce nitrobenzene to phenylamine. [2]

2.2 State the temperature needed to make a stable diazonium salt. [1]

2.3 Give the reagents and conditions for converting nitrobenzene into phenylamine. [3]

2.4 State why the diazotisation must be carried out below 10 °C. [2]

2.5 Explain why phenylamine is a weaker base than ethylamine. [3]

3 Exam-style questions

3.1 A diazonium salt is made from phenylamine using: [1]

- **A** $NaNO_2$ + dilute acid, below 10 °C
- **B** conc. HNO_3 + conc. H_2SO_4
- **C** Br_2 water
- **D** $LiAlH_4$

3.2 The colour of an azo dye is due to the: [1]

- **A** –OH group
- **B** $-NH_2$ group
- **C** –N=N– group
- **D** benzene ring alone

3.3 Outline the two-step synthesis of phenylamine from benzene, giving the reagents for each step. [3]

3.4 A benzenediazonium salt is coupled with phenol in alkaline solution.

(a) State the type of compound formed. [1]

(b) State **one** common use of such compounds. [1]

3.5 An azo dye is made from benzene in four steps.

(a) Give the reagents and conditions for step 1, the conversion of benzene into nitrobenzene, and name the mechanism. [3]

(b) Give the reagents for step 2 and explain why a second reagent is needed after the reduction. [3]

(c) Give the reagents and conditions for the formation of the diazonium salt, and write its formula. [3]

(d) The diazonium salt is coupled with phenol in alkaline solution. Draw the structure of the azo compound formed. [2]

(e) Explain, in terms of electrons, why azo compounds are coloured. [3]

Solutions

2.1 tin (Sn) and concentrated hydrochloric acid; then NaOH(aq).

2.2 below 10 °C (kept cold in an ice bath).

2.3 Tin and concentrated hydrochloric acid; then an excess of sodium hydroxide; heat under reflux.

2.4 Above about 10 °C the diazonium ion is unstable and decomposes to phenol and nitrogen gas, so the yield is lost.

2.5 In phenylamine the nitrogen's lone pair is delocalised into the benzene ring, so it is less available to accept a proton; in ethylamine the alkyl group releases electron density towards the nitrogen, making the lone pair more available.

3.1 A. $NaNO_2$ + dilute acid below 10 °C makes the diazonium salt.

3.2 C. The –N=N– azo group is responsible for the colour.

3.3 nitrate benzene with conc. HNO_3 + conc. H_2SO_4 to give nitrobenzene; reduce with Sn and conc. HCl; then add NaOH(aq) to free the phenylamine.

3.4 (a) an azo compound / azo dye.
(b) used as a dye (colouring).

3.5 (a) Concentrated nitric acid and concentrated sulfuric acid at about 55 °C; electrophilic substitution.
(b) Tin and concentrated hydrochloric acid; the product of the reduction is the phenylammonium salt, not the free amine, so excess sodium hydroxide is added to liberate phenylamine from it.
(c) Sodium nitrite with dilute hydrochloric acid, below 10 °C; $C_6H_5N_2^+Cl^-$.
(d) Two benzene rings joined by $-N=N-$, with the $-OH$ group para to the azo link on the phenol ring.
(e) The azo group $-N=N-$ joins the two rings into one extended delocalised system; a larger delocalised system has a smaller gap between the energy levels; the gap now corresponds to visible light, which is absorbed, and the complementary colour is seen.

7 **(a)** State the relative acidities of bromoethanoic acid, $BrCH_2COOH$, chloroethanoic acid, $ClCH_2COOH$, ethanoic acid, CH_3COOH and ethanol, CH_3CH_2OH.

Explain your answer.

....
most acidic least acidic

.....

.....

.....

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.....

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[4]

(b) Fig. 7.1 shows the reaction of methylbenzene and ethanedioic acid with $KMnO_4$.

Predict the major carbon-containing product for each of these reactions.

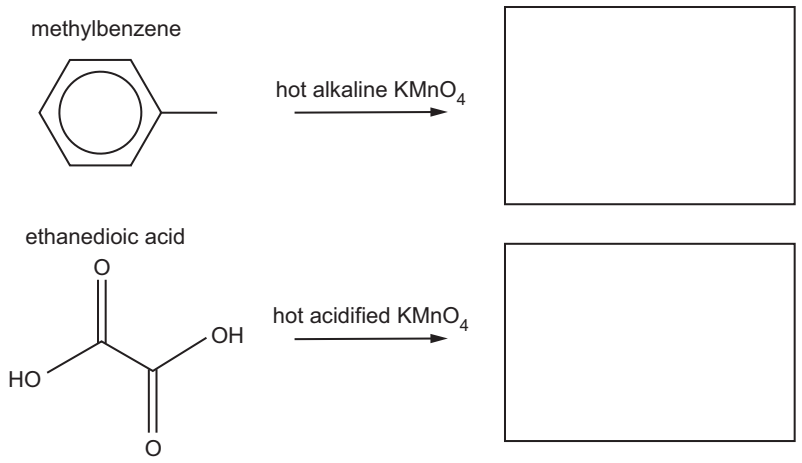
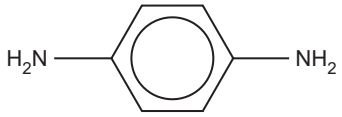


Fig. 7.1

[2]

(c) Polyamide **X** can be synthesised from ethanedioic acid and benzene-1,4-diamine.

benzene-1,4-diamine



(i) Draw the repeat unit of polyamide **X** in the box.

The new functional group formed should be shown displayed.

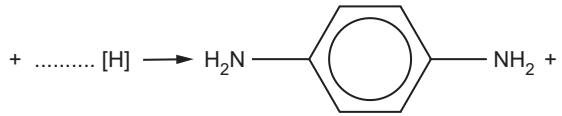
polyamide **X**

[2]

(ii) Benzene-1,4-diamine can be formed by reduction of 1,4-dinitrobenzene.

Complete the equation for this reduction.

[H] represents one atom of hydrogen from a reducing agent.



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[1]

(d) Fig. 7.2 shows the two-step synthesis of the azo compound **W**.

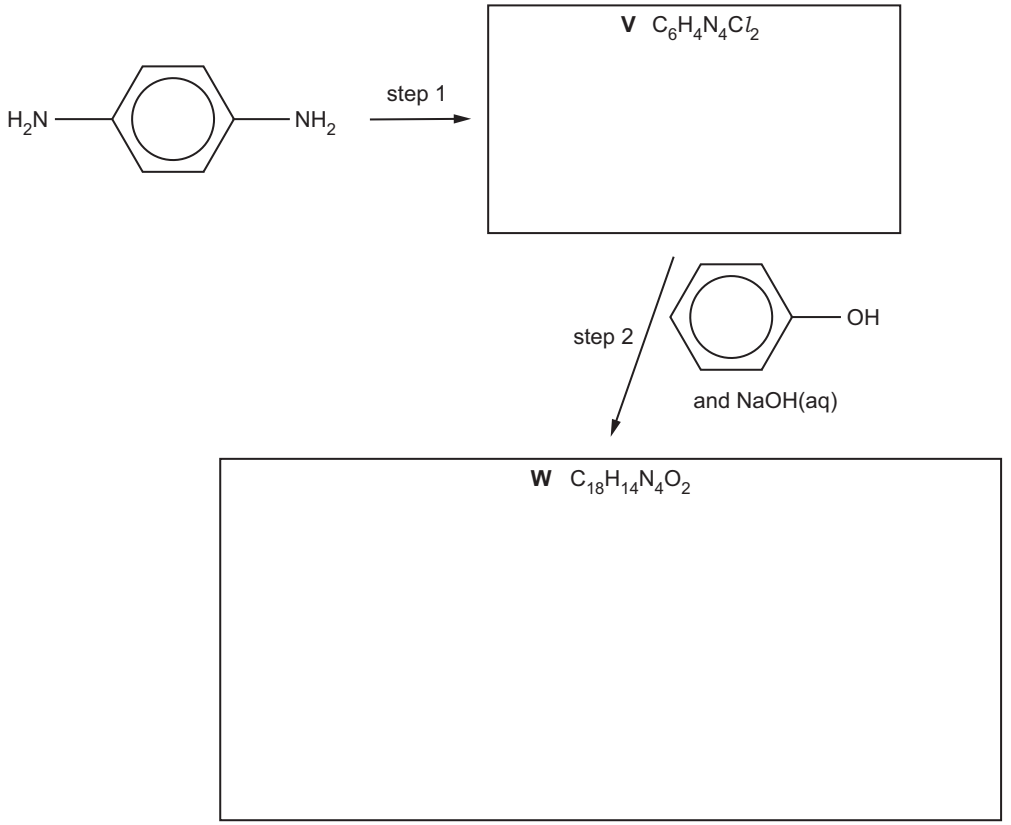

Fig. 7.2

(i) Suggest structures for compounds **V** and **W** and draw them in the boxes in Fig. 7.2. [2]

(ii) Give the reagents and conditions for step 1.

..... [1]

[Total: 12]

9 Compound **X** is made from benzene by the route shown in Fig. 9.1.

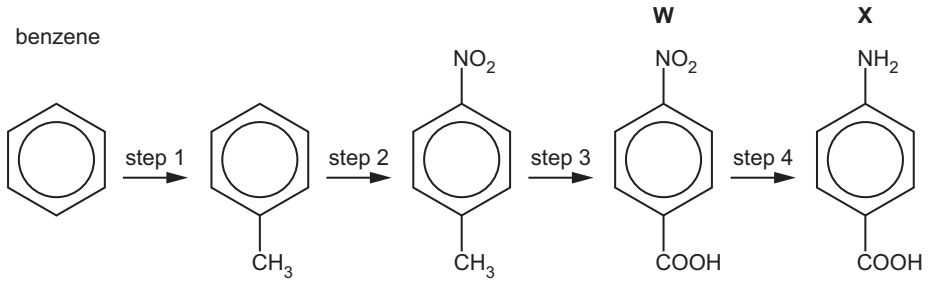

Fig. 9.1

(a) Describe the bonding in benzene, C_6H_6.

Your answer should include:

- the hybridisation of the six carbon atoms
- the types of bond between the carbon atoms
- the orbitals that overlap to produce the bonds between the carbon atoms
- the type of bond between the carbon atoms and the hydrogen atoms
- the orbitals that overlap to produce the bonds between the carbon atoms and the hydrogen atoms.

.....

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.....

.....

.....

.....

..... [3]

(b) Describe the reagents and conditions required for step 1 in Fig. 9.1.

.....

..... [1]

(c) In step 1 of Fig. 9.1 benzene reacts with $^+CH_3$.

Complete Fig. 9.2 to show the mechanism for this reaction, including:

- the movement of electron pairs using curly arrows
- the structure of the intermediate involved.

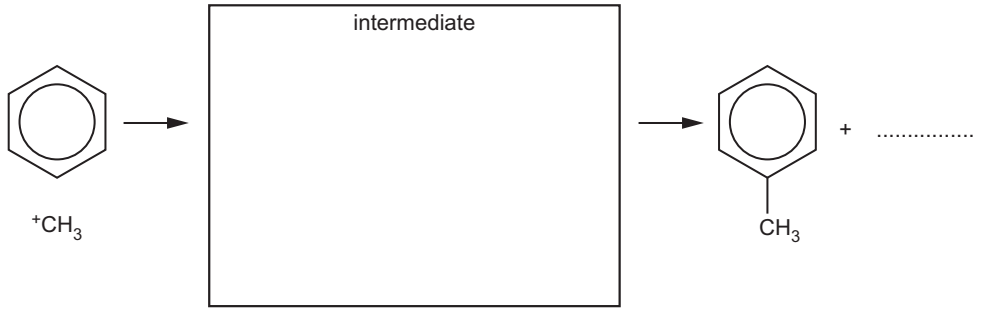


Fig. 9.2

[3]

(d) Describe the reagents and conditions required for step 2 of Fig. 9.1.

.....

..... [2]

(e) Identify the reagents required for step 3 of Fig. 9.1. Compound **W** is the product of this step.

..... [1]

(f) Name compound **W**.

..... [1]

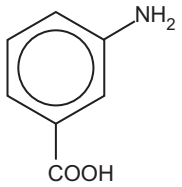
(g) The reagents commonly used for step 4 will **not** reduce the –COOH group.

Identify the reagents and conditions required for step 4 of Fig. 9.1.

..... [1]

(h) Benzene can also be used as a starting material to make compound **Y**.

compound **Y**



Describe how the route described in Fig. 9.1 (repeated below) can be changed to give compound **Y** instead of compound **X**.

Explain your answer.

.....

.....

.....

..... [2]

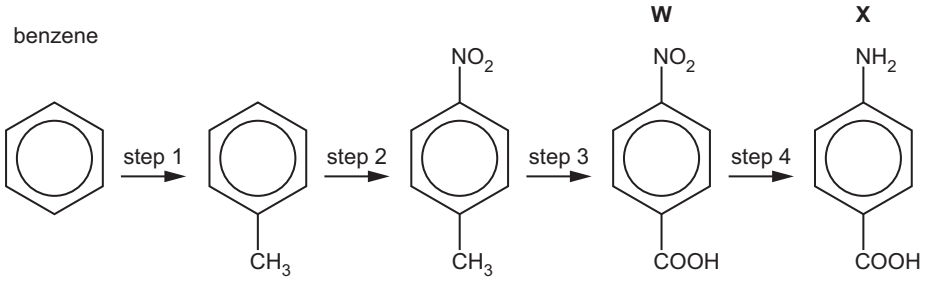


Fig. 9.1

[Total: 14]

Important values, constants and standards

molar gas constant	$R = 8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^{4}\,\text{C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23}\,\text{mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,\text{C}$
molar volume of gas	$V_m = 22.4\,\text{dm}^3\,\text{mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,\text{dm}^3\,\text{mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,\text{mol}^2\,\text{dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,\text{kJ kg}^{-1}\,\text{K}^{-1}$ ($4.18\,\text{J g}^{-1}\,\text{K}^{-1}$)

The Periodic Table of Elements

Group 1	2												13	14	15	16	17	18
												1 H hydrogen 1.0						2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0												5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3												13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –	118 Og oganesson –

Key

atomic number
atomic symbol
name
relative atomic mass

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

A-LEVEL CHEMISTRY • EXERCISE SHEET

34.3 Amides

Name: _____ Class: _____ Date: _____ **Total: 23 marks**

KEY WORDS amides 酰胺 • hydrolysis 水解 • amine 胺 • reduction 还原 • ammonia 氨

Objective

Build the skills to answer exam questions on **amides** 酰胺 — making them, their **hydrolysis** 水解 and reduction, and why an amide is a very weak base.

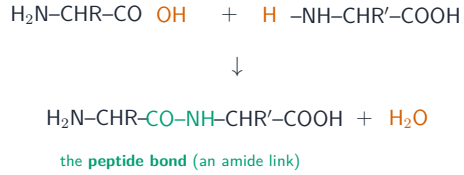
You must be able to:

- make an amide from an acyl chloride and ammonia/an amine
- give the products of acid and alkaline hydrolysis of an amide
- explain why an amide is a much weaker base than an amine

1 Worked examples

■ **Reactions of amides**

An amide is made from an acyl chloride with ammonia or an amine (+ HCl)



Amides include the peptide bond

- **make it:** acyl chloride + NH_3 (or amine) → amide + HCl.
- **acid hydrolysis:** amide + H^+/water → carboxylic acid + ammonium salt.
- **alkaline hydrolysis:** amide + OH^- → carboxylate salt + ammonia.
- **reduction:** $LiAlH_4$ reduces the C=O to give an amine.
- an amide is a **very weak base** — its N lone pair is delocalised onto the C=O, so it cannot accept an H^+.

2 Practice

2.1 Give the two reagents used to make ethanamide. [2]

2.2 Name the organic product of reducing ethanamide with $LiAlH_4$. [1]

3 Exam-style questions

3.1 Acid hydrolysis of ethanamide gives ethanoic acid and: [1]

- **A** ethylamine
- **B** an ammonium salt
- **C** ethanol
- **D** ethene

3.2 An amide is a much weaker base than an amine because the nitrogen lone pair is: [1]

- **A** removed completely
- **B** delocalised onto the adjacent C=O group
- **C** used in a C–H bond
- **D** more available

3.3 Ethanamide is hydrolysed by hot aqueous NaOH.

(a) Name the two products. [2]

(b) Write the equation. [2]

3.4 Explain why ethanamide is a far weaker base than ethylamine. [2]

3.5 *N*-methylethanamide, $CH_3CONHCH_3$, is a secondary amide.

(a) Name the two compounds that react together to make it, and state why an acyl chloride is preferred to the carboxylic acid. [3]

(b) The amide is refluxed with (i) dilute hydrochloric acid and (ii) aqueous sodium hydroxide. Give the organic products in each case. [4]

(c) The amide is reduced with $LiAlH_4$ in dry ether. Name the product and give the equation using [H]. [2]

(d) Explain why an amide is a far weaker base than an amine. [3]

Solutions

2.1 ethanoyl chloride; ammonia, NH_3.

2.2 ethylamine.

3.1 B. Acid hydrolysis gives ethanoic acid and an ammonium salt.

3.2 B. The N lone pair is delocalised onto the neighbouring C=O group.

3.3 (a) sodium ethanoate and ammonia.
(b) $CH_3CONH_2 + NaOH \rightarrow CH_3COONa + NH_3$.

3.4 in ethanamide the nitrogen lone pair is delocalised onto the C=O group; so it is not available to accept an H^+, whereas in ethylamine the lone pair is fully available.

3.5 (a) Ethanoyl chloride and methylamine; the acyl chloride reaction is fast and goes to completion, whereas the carboxylic acid would simply form an ammonium salt in an acid–base reaction.
(b) (i) With acid: **ethanoic acid** and the salt **methylammonium chloride**. (ii) With alkali: **sodium ethanoate** and **methylamine** — the base deprotonates the acid and frees the amine.
(c) $CH_3CONHCH_3 + 4[H] \rightarrow CH_3CH_2NHCH_3 + H_2O$; the product is the secondary amine *N*-methylethylamine.
(d) In an amide the nitrogen lone pair is **delocalised** onto the adjacent carbonyl oxygen; it is therefore not available to accept a proton; in an amine the lone pair sits on the nitrogen alone, with no electron-withdrawing carbonyl beside it, so it is readily donated.

7 **(a)** State the relative acidities of bromoethanoic acid, $BrCH_2COOH$, chloroethanoic acid, $ClCH_2COOH$, ethanoic acid, CH_3COOH and ethanol, CH_3CH_2OH.

Explain your answer.

....
most acidic least acidic

.....

.....

.....

.....

.....

.....

.....

[4]

(b) Fig. 7.1 shows the reaction of methylbenzene and ethanedioic acid with $KMnO_4$.

Predict the major carbon-containing product for each of these reactions.

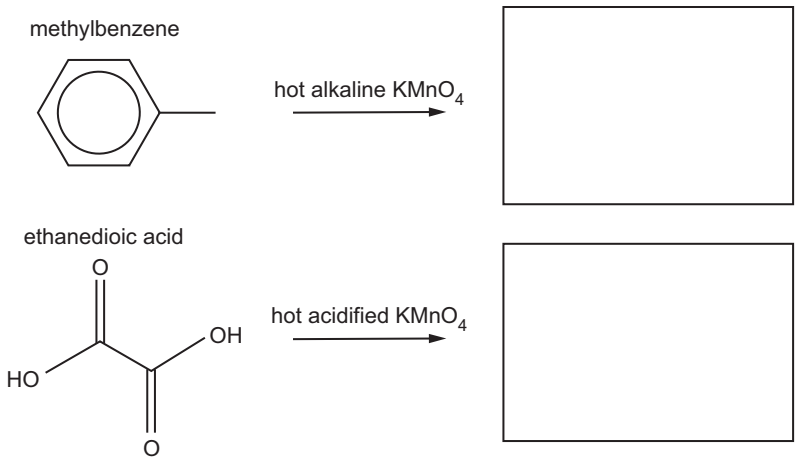
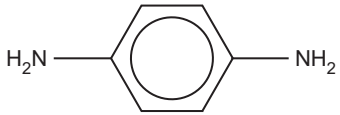


Fig. 7.1

[2]

(c) Polyamide **X** can be synthesised from ethanedioic acid and benzene-1,4-diamine.

benzene-1,4-diamine



(i) Draw the repeat unit of polyamide **X** in the box.

The new functional group formed should be shown displayed.

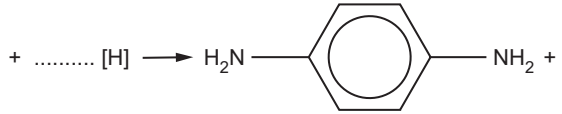
polyamide **X**

[2]

(ii) Benzene-1,4-diamine can be formed by reduction of 1,4-dinitrobenzene.

Complete the equation for this reduction.

[H] represents one atom of hydrogen from a reducing agent.



....

[1]

(d) Fig. 7.2 shows the two-step synthesis of the azo compound **W**.

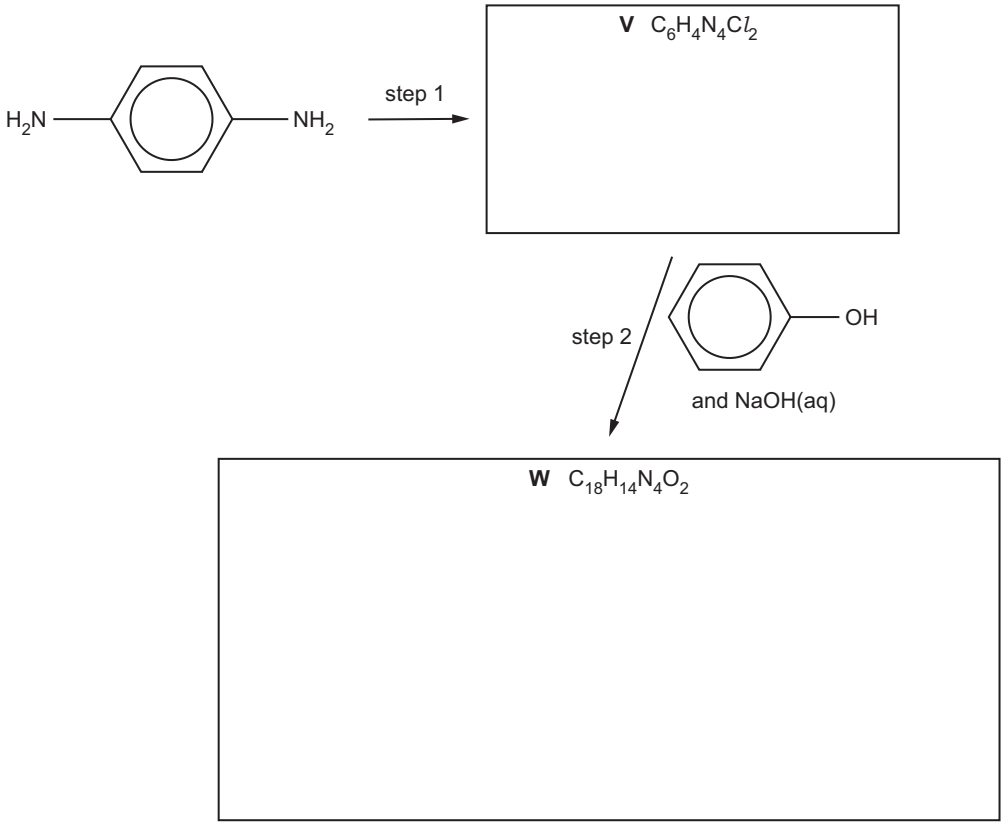


Fig. 7.2

(i) Suggest structures for compounds **V** and **W** and draw them in the boxes in Fig. 7.2. [2]

(ii) Give the reagents and conditions for step 1.

..... [1]

[Total: 12]

9 **(a)** Explain why amides are much weaker bases than amines.

.....

.....

.....

..... [2]

(b) Fig. 9.1 shows the preparation of 2-phenylethylamine, $C_6H_5CH_2CH_2NH_2$, by three different routes.

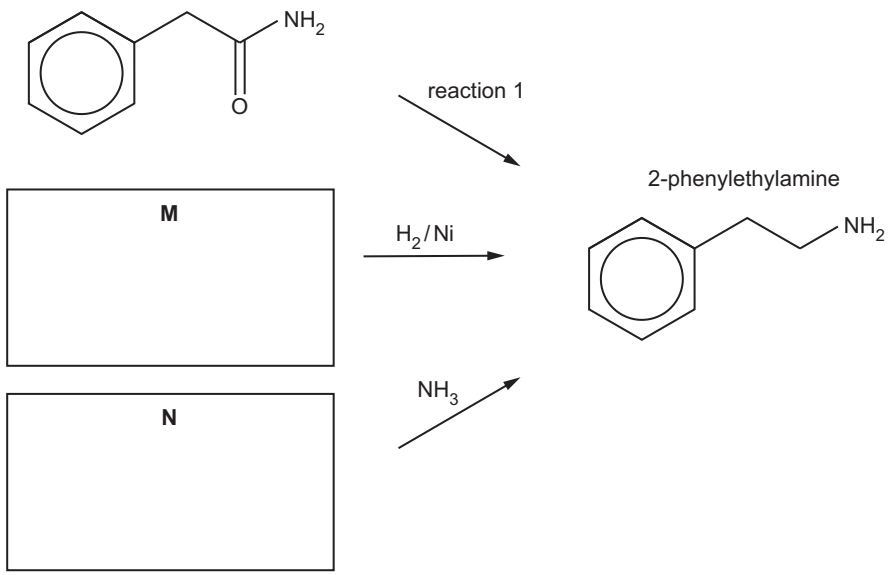


Fig. 9.1

(i) Suggest structures for compounds **M** and **N** and draw them in the boxes in Fig. 9.1. [2]

(ii) Give the reagents and conditions for reaction 1.

..... [1]

(c) Fig. 9.2 shows compound **H** which is a useful starting material in organic synthesis.

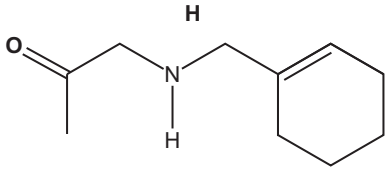


Fig. 9.2

H contains an alkene and an amine functional group.

Name the **other** functional group and give the classification of the amine group in **H**.

other functional group in **H** .....

classification of amine .....

[1]

(d) Ozonolysis involves the oxidative cleavage of a C=C bond in alkenes using ozone, O_3, as shown in Fig. 9.3.

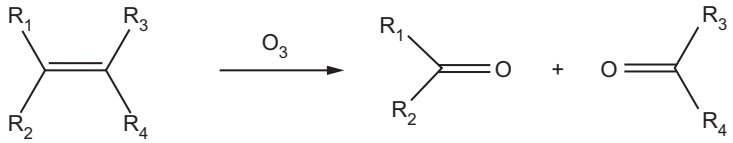


Fig. 9.3

Fig. 9.4 shows the first step in this reaction which involves the formation of an ozonide intermediate.

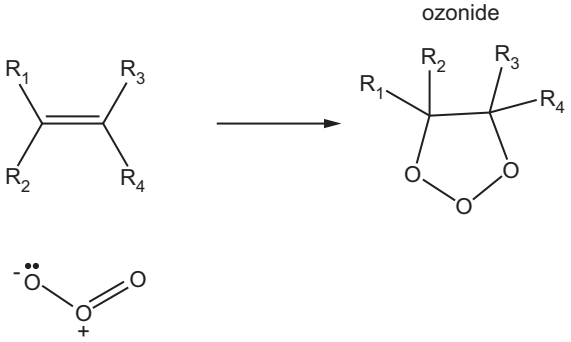
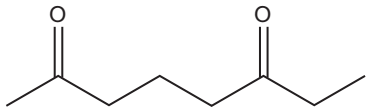


Fig. 9.4

(i) On Fig. 9.4, draw **three** curly arrows to complete the mechanism of this step. [2]

(ii) **L** is formed from alkene **K**, C_8H_{14}, by a similar reaction to that shown in Fig. 9.3.

L



Suggest the structure of **K**.

K C_8H_{14}

[1]

[Total: 9]

Important values, constants and standards

molar gas constant	$R = 8.31\,J\,K^{-1}\,mol^{-1}$
Faraday constant	$F = 9.65 \times 10^4\,C\,mol^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23}\,mol^{-1}$
electronic charge	$e = -1.60 \times 10^{-19}\,C$
molar volume of gas	$V_m = 22.4\,dm^3\,mol^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0\,dm^3\,mol^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14}\,mol^2\,dm^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18\,kJ\,kg^{-1}\,K^{-1}$ ($4.18\,J\,g^{-1}\,K^{-1}$)

The Periodic Table of Elements

Group 1	2																	18
												13	14	15	16	17		2 He helium 4.0
3 Li lithium 6.9	4 Be beryllium 9.0											5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0		10 Ne neon 20.2
11 Na sodium 23.0	12 Mg magnesium 24.3	3	4	5	6	7	8	9	10	11	12	13 Al aluminium 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5		18 Ar argon 39.9
19 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9		36 Kr krypton 83.8
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9		54 Xe xenon 131.3
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –		86 Rn radon –
87 Fr francium –	88 Ra radium –	89–103 actinoids	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	113 Nh nihonium –	114 Fl flerovium –	115 Mc moscovium –	116 Lv livermorium –	117 Ts tennessine –		118 Og oganesson –

Key

atomic number
atomic symbol
name
relative atomic mass

1 H hydrogen 1.0

lanthanoids	57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0
actinoids	89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –

A-LEVEL CHEMISTRY • EXERCISE SHEET

34.4 Amino acids

Name: _____ Class: _____ Date: _____ **Total: 10 marks**

KEY WORDS amino acids 氨基酸 • isoelectric point 等电点 • electrophoresis 电泳 • peptide bond 肽键 • zwitterions 两性离子

Objective

Build the skills to answer exam questions on **amino acids** 氨基酸 — **zwitterions** 两性离子, the **isoelectric point** 等电点, **peptide bonds** 肽键 and **electrophoresis** 电泳.

You must be able to:

- explain how an amino acid forms a zwitterion and how its charge changes with pH
- describe peptide-bond formation by condensation
- explain how electrophoresis separates amino acids

1 Worked examples

■ Charge with pH; peptide bonds

Charge depends on pH: positive in acid, the neutral zwitterion at the isoelectric point, negative in alkali

- in **acid** (low pH): $-COO^-$ gains H^+ → ion is **positive**.
- in **alkali** (high pH): $-NH_3^+$ loses H^+ → ion is **negative**.
- at the **isoelectric point**: mostly the neutral zwitterion, **no net charge**.

Two amino acids condense (losing water) to form a peptide (amide) bond

2 Practice

2.1 State what is meant by a **zwitterion**. [1]

2.2 Name the type of bond formed when two amino acids join. [1]

3 Exam-style questions

3.1 At a pH **below** its isoelectric point, an amino acid carries an overall: [1]

- **A** positive charge
- **B** negative charge
- **C** zero charge
- **D** double negative charge

3.2 In electrophoresis, an amino acid that is **negatively** charged moves towards the: [1]

- **A** negative electrode
- **B** positive electrode
- **C** neither electrode
- **D** both electrodes

3.3 Explain, using equations or structures, how the charge on the amino acid glycine (H_2NCH_2COOH) changes between low pH and high pH. [3]

3.4 Two amino acids are mixed and held at a pH equal to the isoelectric point of one of them. Explain what happens to each in electrophoresis. [3]

Solutions

2.1 an ion with both a positive ($–NH_3^+$) and a negative ($–COO^-$) charge but no overall charge.

2.2 a peptide bond (an amide link).

3.1 A. Below the isoelectric point, extra H^+ gives an overall positive charge.

3.2 B. A negative ion is attracted to the positive electrode.

3.3 at low pH the $–COO^-$ is protonated to –COOH, giving $H_3N^+CH_2COOH$, overall positive; at high pH the $–NH_3^+$ loses H^+ to give $H_2NCH_2COO^-$, overall negative; between them lies the zwitterion $H_3N^+CH_2COO^-$ at the isoelectric point.

3.4 the amino acid at its isoelectric point is a neutral zwitterion, so it does not move; the other amino acid is charged at that pH; so it migrates towards the oppositely charged electrode, separating the two.

8 Asparagine and aspartic acid are two naturally occurring amino acids. Their structures and isoelectric points are shown in Table 8.1.

Table 8.1

amino acid	structure	isoelectric point
asparagine	$HOOCCH(NH_2)CH_2CONH_2$	5.41
aspartic acid	$HOOCCH(NH_2)CH_2COOH$	2.77

(a) Define isoelectric point.

.....

..... [1]

(b) Draw the structures of asparagine and aspartic acid at pH 2.

asparagine at pH 2	aspartic acid at pH 2

[2]

(c) Asparagine and aspartic acid are treated separately with an excess of $LiAlH_4$.

Draw the structures of the organic products of these reactions.

product of asparagine treated with an excess of $LiAlH_4$	product of aspartic acid treated with an excess of $LiAlH_4$

[2]

(d) Propanedioic acid, $HOOCCH_2COOH$, is treated with an excess of thionyl chloride, $SOCl_2$. Propanedioyl chloride, $ClOCCH_2COCl$, is formed.

(i) Write an equation for this reaction.

..... [1]

(ii) Propanedioyl chloride reacts with an excess of asparagine to form compound **G** with molecular formula $C_{11}H_{16}N_4O_8$.

Each molecule of compound **G** has four amide groups.

Draw the structure of compound **G**.

Compound **G**, $C_{11}H_{16}N_4O_8$

[2]

(e) Asparagine is hydrolysed with an excess of hot NaOH(aq).

Draw the structure of the organic product of this reaction.

[2]

(f) A polymer can form from asparagine, $HOOCCH(NH_2)CH_2CONH_2$, as the only monomer.

Draw a length of the polymer chain containing **three** monomer residues.

Clearly label the repeat unit of the polymer on your diagram.

[3]

(g) Aspartic acid exists in two optically active forms.

(i) Plane polarised light is passed through pure samples of these two optically active forms in solutions of the same concentration.

Describe **two** similarities and **one** difference in their effect on the plane polarised light.

similarities .....

.....

difference .....

.....

[2]

(ii) Give the term used to describe a mixture of equal amounts of the two optically active forms.

..... [1]

[Total: 16]

Question 9 starts on page 20.