NAME DATE STARTED TARGET END DATE

GCE A LEVEL — CHEMISTRY UNIT 4 QUESTION PACK

1095-01 (Legacy CH4) · New spec Unit 4 Topic 4 · A2 unit, first sat 2017, 80 marks, 1h 45min paper

REVISE.wales

CHEMISTRY — UNIT 4 · Amines & Multi-step Synthesis Routes

Topics 4.5 & 4.7 — Amines as nucleophiles and bases, diazonium salts, azo dyes, and devising multi-step organic synthesis routes

Primary, secondary and tertiary amines as Brønsted bases and nucleophiles, preparation from nitriles, halogenoalkanes and nitro compounds, diazotisation of phenylamine, azo coupling for dyes, and designing two- to four-step synthesis routes by combining functional group interconversions.

Legacy 2008 specification

Estimated time for entire question pack: ~1 h 23 min

Derived from the legacy CH4 paper's pace of ~1.3 min/mark, padded for long-prose and synthesis answers (52 marks over 4 questions).

*You are advised to **not** attempt to complete all of this in one sitting.*

ABOUT THIS QUESTION PACK

This is a **comprehensive practice question pack**, not a single mock paper. It contains every question from the legacy WJEC CH4 papers (2008 modular spec, Jan 2010 – Jun 2016) that maps onto the new-spec A2 Unit 4 Topic 4.5 & 4.7.

Questions are ordered by source paper date.

INSTRUCTIONS

Use black ink or black ball-point pen. Show all working — quality of written communication will affect marks. A calculator is allowed. You will need the WJEC Periodic Table / Data Booklet.

For Examiner's use only

Q	Source	Max	Mark
1	Jun 10 Q1	10	
2	Jun 10 Q4	20	

Q	Source	Max	Mark
3	Jun 12 Q2	10	
4	Jun 15 Q2	12	
Total		**52**	

Amines & Multi-step Synthesis Routes — what the new spec asks

WJEC GCE A Level Chemistry (from 2015) · Unit 4: Organic Chemistry & Analysis · Topic 4.5 & 4.7.

Amines as bases

- $RNH_2 + H^+ \rightharpoonup RNH_3^+$.
- Aliphatic amines stronger bases than NH_3 (+I from alkyl); aromatic weaker (lone pair into ring).
- Order of base strength: 2° aliphatic > 1° aliphatic > NH_3 > aromatic amine.
- Form salts with acids; salts soluble in water (used for drug formulation).

Amines as nucleophiles

- RNH_2 attacks δ^+ C in halogenoalkanes → substituted amines (+ HX).
- Excess amine to limit further substitution to 2° / 3° / quaternary salts.
- RNH_2 + acyl chloride → amide + HCl (rapid, irreversible).
- Aniline + CH_3COCl → N-phenylethanamide (acetanilide).

Preparation of amines

- Halogenoalkane + NH_3 (ethanol, sealed, heat) → primary amine + HX.
- Nitrile reduction: RCN + 4[H] ($LiAlH_4$) → RCH_2NH_2.
- Nitro compound reduction (aromatic): Sn + conc. HCl, reflux, then NaOH → aniline.
- Hofmann reaction (amides): $RCONH_2 + Br_2$/NaOH → $RNH_2 + CO_3^{2-}$.

Diazonium salts & azo dyes

- Aniline + $NaNO_2$ + dilute HCl, <10 °C → benzenediazonium chloride $C_6H_5N_2^+Cl^-$.
- Diazonium ion stabilised by ring delocalisation; aliphatic equivalents decompose to N_2.
- Couples with phenoxide (alkaline) or amine to give azo dye (–N=N– chromophore).
- Azo dyes: brightly coloured because of extended conjugation; used in food and textiles.

Synthesis route planning

- Identify FG transformations between start and target.
- Common interconversions: alcohol ↔ haloalkane ↔ nitrile ↔ amine ↔ carboxylic acid.
- Carbon chain extension: RX → RCN (KCN/EtOH) → RCH_2NH_2 or RCOOH.
- Carbon chain reduction: RCOOH → RCH_2OH ($LiAlH_4$); RCOOH → RH (decarboxylation, rare).

Aromatic route patterns

- Benzene → nitrobenzene (HNO_3/H_2SO_4) → aniline (Sn/HCl, NaOH).
- Aniline → diazonium → phenol (warm water) or azo dye (couple with phenoxide).
- Methylbenzene → benzoic acid (hot conc. $KMnO_4$).
- Benzene → phenylethanone ($CH_3COCl + AlCl_3$, Friedel-Crafts).

Crib sheet »

Amines & Multi-step Synthesis Routes in one page

Quick-reference notes — revisit before each question.

Amine basicity

$RNH_2 + H_2O \rightharpoonup RNH_3^+ + OH^-$.
Aliphatic amine > NH_3 > aromatic amine (lone pair delocalised into ring ⇒ less available).

Amine prep

RX + NH_3 (excess, ethanol, heat in sealed tube).
RCN + $LiAlH_4$ → RCH_2NH_2.
$ArNO_2$ + Sn/HCl, then NaOH → $ArNH_2$.

Diazotisation

$ArNH_2 + HNO_2$ (HCl + $NaNO_2$) at <10 °C → $ArN_2^+Cl^-$. Above 10 °C: decomposes → phenol + N_2.

Azo coupling

ArN_2^+ + phenoxide (alkaline) → $ArN{=}N{-}C_6H_4{-}OH$ azo dye. Extended conjugation absorbs visible light ⇒ intense colours.

Chain extension

R–Br → R–CN (KCN, EtOH, reflux) adds one carbon. Then RCN → RCOOH (acid hydrolysis) or RCH_2NH_2 ($LiAlH_4$).

Synthesis sequencing

Plan backward from target. Identify each FG change; chain length; whether to use protecting groups (rare here). Avoid harsh conditions that destroy other groups in the molecule.

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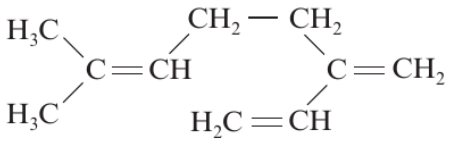
SECTION A

Answer **all** *questions in the spaces provided.*

1. *(a)* Terpenes are the primary constituents of the essential oils of many types of plants and flowers.
An example is myrcene, one of the most important chemicals used in the perfume industry because of its pleasant odour. It has the structure shown below.



(i) State the molecular formula of myrcene. [1]

.....

(ii) Draw the **skeletal** formula of myrcene. [1]

(iii) Myrcene reacts with hydrogen to form a saturated hydrocarbon in the same way as alkenes of general formula C_nH_{2n}.

I. Explain what is meant by the term *saturated* hydrocarbon. [1]

.....

.....

II. Using molecular formulae write an equation for this reaction. [1]

.....

Examiner only

(iv) Another terpene, α-farnasene, is responsible for the characteristic odour of green apples.
A 0.100 mol sample of α-farnasene reacted with 8.96 dm^3 of hydrogen to form a saturated hydrocarbon $C_{15}H_{32}$.
(1 mole of gas molecules occupy 22.4 dm^3 under these conditions.)

Calculate how many double bonds there are in each molecule of α-farnasene. [2]

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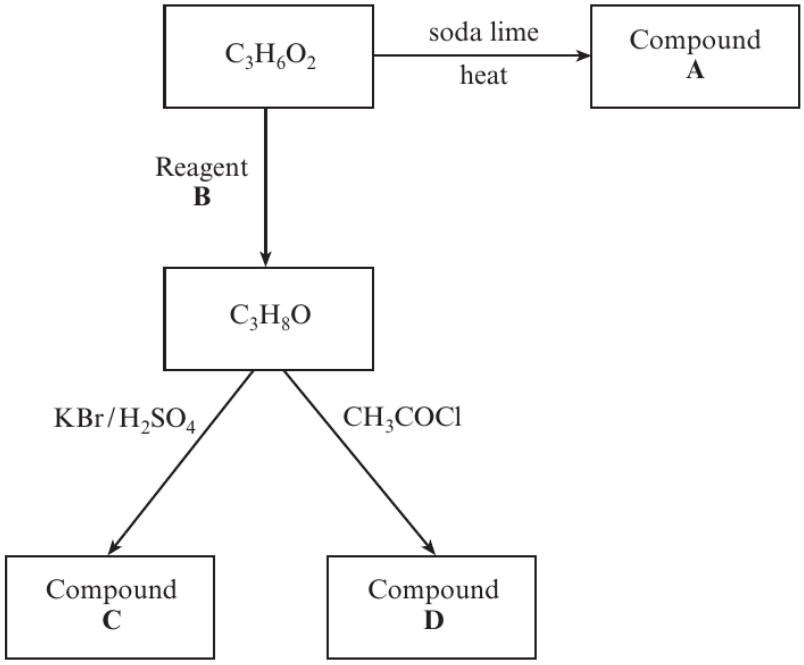
Examiner only

(b) Study the reaction scheme shown below:



(i) State the name of compound **A**. [1]

.....

(ii) Give the formula of reagent **B**. [1]

.....

(iii) Draw the displayed formula of compound **C**. [1]

(iv) State the **name** of compound **D**. [1]

.....

Total [10]

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SECTION B

Answer **both** *questions in the separate answer book provided.*

4. *(a)* The reaction between but-1-ene and hydrogen bromide produces a mixture of **three** isomers.

(i) Draw the displayed formula of each of the three isomers. [3]

(ii) Outline how each of the isomers can be distinguished from one another. [3]

(QWC) [1]

(b) (i) Ethylamine can be produced by the reaction of ammonia with chloroethane.

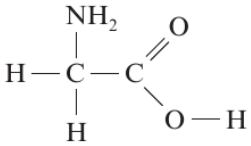
I. Write an equation for this reaction. [1]

II. Classify the type of reaction taking place. [1]

(ii) Phenylamine cannot be prepared in this way. Name the starting material and reagent(s) used to prepare phenylamine in a laboratory. [2]

(iii) Give one chemical test, including reagent(s), condition(s) and expected observations, which would distinguish between ethylamine and phenylamine. [3]

(c) Amino acids also contain an amine group. The simplest amino acid, aminoethanoic acid (glycine) has the formula



(i) Draw the displayed formula of 2-aminopropanoic acid (alanine). [1]

(ii) A dipeptide can be formed by reacting two amino acids. Draw the displayed formulae of the two different dipeptides which can be made by combining glycine and alanine. [2]

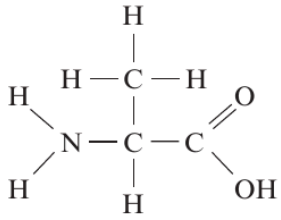
(iii) Proteins are natural polypeptides. Explain briefly what is meant by primary, secondary and tertiary protein structure. [3]

Total [20]

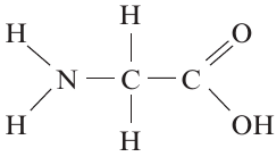
Examiner only

2. Proteins and polypeptides are natural polyamides built up from α-amino acids.

(a) Two naturally-occurring α-amino acids are alanine and glycine.

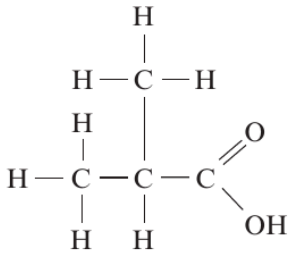


alanine
(2-aminopropanoic acid)



glycine
(2-aminoethanoic acid)

(i) Alanine *(2-aminopropanoic acid)* has a melting temperature of 258 °C whereas the similar compound 2-methylpropanoic acid melts at –46 °C.



2-methylpropanoic acid

Explain why the value for alanine is so much higher than that of 2-methylpropanoic acid. [2]

.....

.....

.....

(ii) Draw the **two** possible dipeptides that can form when one molecule of glycine combines with one molecule of alanine. [2]

(iii) Circle the peptide linkage in **one** of your dipeptides. [1]

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(b) Give **one** use of proteins or polypeptides in biological systems. [1]

.....

(c) One laboratory synthesis of amino acids involves the reaction between an aldehyde and hydrogen cyanide, HCN, as the first step before the amino group is introduced into the molecule.
For a general aldehyde, R-CHO, draw the mechanism of the reaction that occurs between this molecule and HCN. [3]

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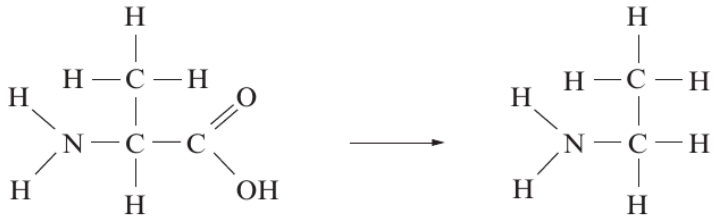
(d) Amino acids can be converted to amines in a one-step process, as shown below.



Name the reagent required for this reaction. [1]

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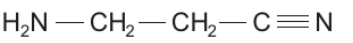
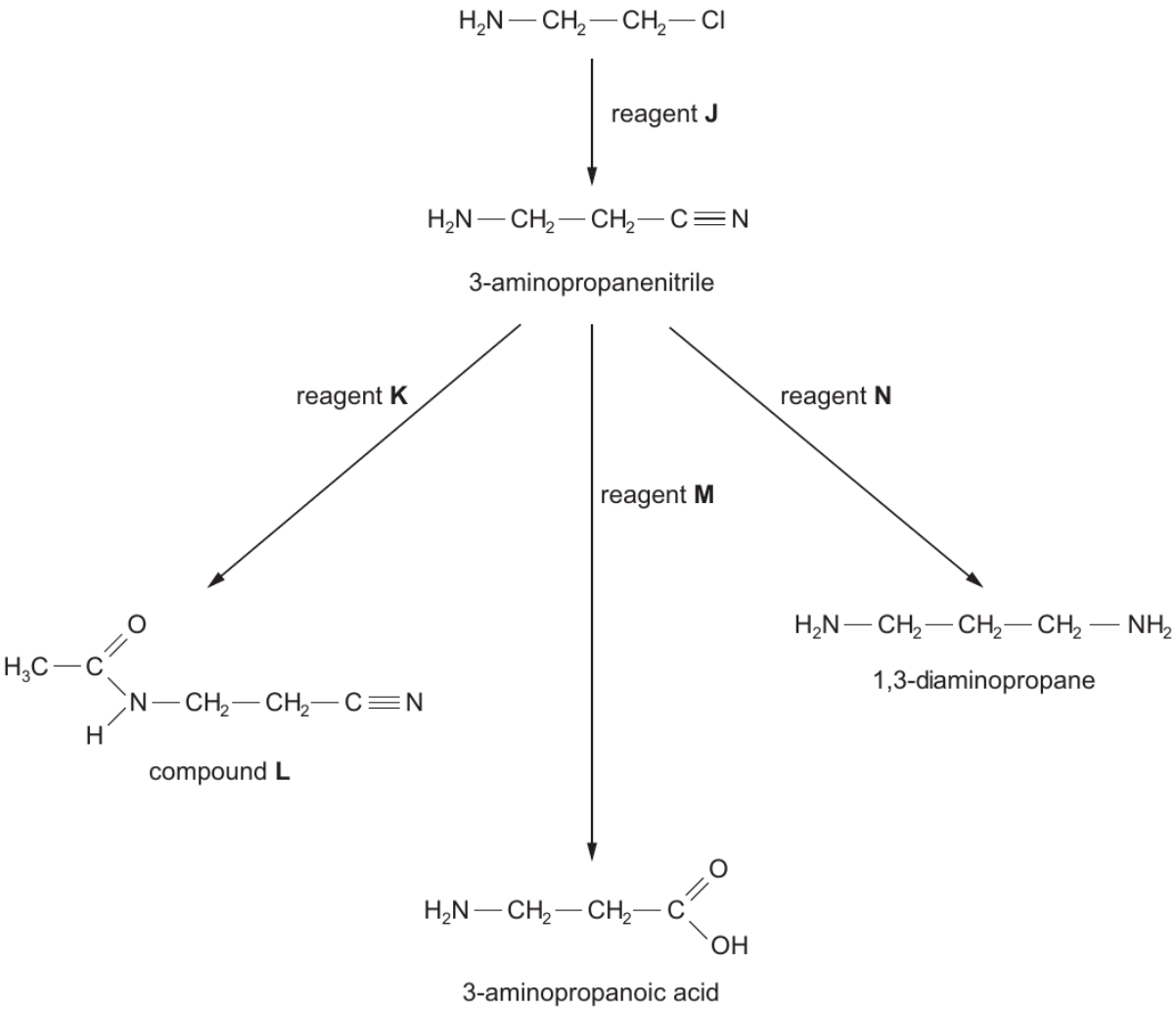
Total [10]

Turn over.

2. *(a)* Seeds of the sweet pea plant contain 3-aminopropanenitrile.



One method of preparation of this compound and some of its reactions are outlined below.



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(i) State the name of reagent **J**. [1]

.....

(ii) Give the displayed formula of reagent **K** that is used to produce compound **L** from 3-aminopropanenitrile. [1]

(iii) State the name of reagent **M**, which is used in aqueous solution. [1]

.....

(iv) Although 3-aminopropanoic acid is not an α-amino acid, it exists as a zwitterion in a similar way to an α-amino acid.

Give the displayed formula of the zwitterion form of 3-aminopropanoic acid. [1]

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(v) 3-Aminopropanoic acid and compound **X** are isomers of formula $C_3H_7NO_2$. However, only compound **X** produces a silver mirror when reacted with Tollens' reagent. Suggest a displayed formula for compound **X**. [1]

(vi) State the formula of reagent **N**. [1]

.....

(vii) State why amines such as 1,3-diaminopropane are able to act as bases. [1]

.....

.....

Turn over.

Examiner only

(b) Care has to be taken when collecting fungi for consumption as many of them contain poisonous compounds. An Asian mushroom contains a very toxic compound **G**. Some information about compound **G** is given below.

- It is an alicyclic compound (a **ring** compound of carbon atoms that is not aromatic)
- Its empirical formula is C_2H_2O
- It is an unsaturated compound
- It contains one carboxylic acid group, whose carbon atom is not part of the ring structure
- All the oxygen atoms present are in the carboxylic acid group
- The proton NMR spectrum shows 3 peaks whose relative peak areas are 1:1:2

Answer the questions below, which lead you through the information to help you find the displayed formula for compound **G**.

(i) Give the molecular formula for compound **G**. ..... [1]

(ii) Since one of the carbon atoms present is not part of the ring structure, the number of carbon atoms in the ring is ..... . [1]

(iii) Compound **G** is an unsaturated compound and therefore the ring must contain the functional group ..... . [1]

(iv) The peak areas in the NMR spectrum are 1:1:2. The carboxylic acid group proton is responsible for a peak area 1.

The remaining peak area ratio 1:2 suggests that .....

.....

.....

[1]

(v) Use the information from parts (i) to (iv) to suggest the displayed formula for compound **G**. [1]

Total [12]

12

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END OF QUESTION PACK

4 questions · 52 marks · ~1 h 23 min
Source: WJEC CH4 (2008 modular spec, Jan 2010 – Jun 2016)
Curated for WJEC Chemistry 2015 spec A2 Unit 4 — Topic 4 (4.5 & 4.7)