

Surname	Centre Number	Candidate Number
Other Names		2



GCE A level

1094/01

CHEMISTRY CH4

A.M. WEDNESDAY, 13 June 2012

1³/₄ hours

FOR EXAMINER'S USE ONLY		
Section	Question	Mark
A	1	
	2	
	3	
B	4	
	5	
TOTAL MARK		

ADDITIONAL MATERIAL

In addition to this examination paper, you will need:

- a calculator;
 - an 8 page answer book;
 - a **Data Sheet** which contains a **Periodic Table** supplied by WJEC.
- Refer to it for any **relative atomic masses** you require.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen.

Write your name, centre number and candidate number in the spaces at the top of this page.

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

Section B Answer **both** questions in **Section B** in a separate answer book which should then be placed inside this question-and-answer book.

Candidates are advised to allocate their time appropriately between **Section A (40 marks)** and **Section B (40 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

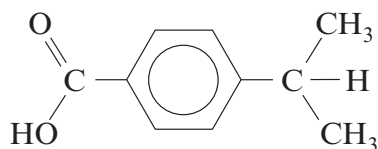
Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

You are reminded that marking will take into account the Quality of Written Communication in all written answers.

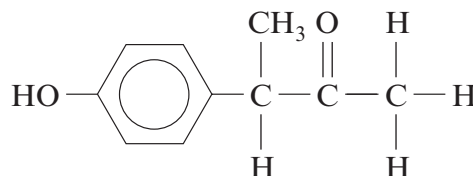
SECTION A

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

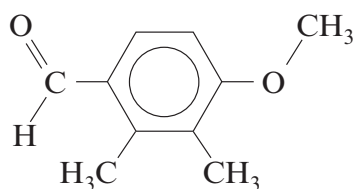
1. This question focuses on the chemistry of some of the many compounds which share the molecular formula $C_{10}H_{12}O_2$. Four compounds with this formula are shown below.



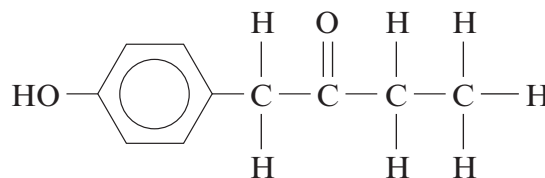
compound W



compound X



compound Y



compound Z

- (a) Draw an **ester** which is an isomer of the compounds above.

[1]

- (b) Only one of the compounds shown can exhibit optical isomerism.

- (i) Identify which compound can exhibit optical isomerism. [1]
- (ii) Indicate the chiral centre in this molecule by labelling it with an asterisk (*). [1]
- (iii) State how the two enantiomers of this compound can be distinguished. [1]

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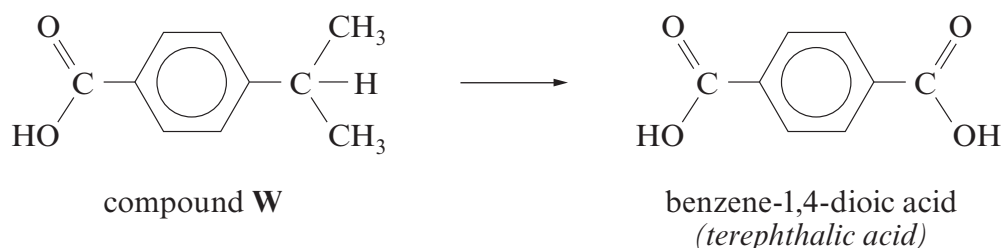
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- (c) The four compounds **W**, **X**, **Y** and **Z** were tested using a series of reagents. For each of the tests listed below, describe what would be expected to be observed in a positive test. Indicate which compounds would be expected to give a positive result. [6]

All the tests listed will give positive results with at least one compound.

<i>Reagent(s)</i>	<i>Observation if the test is positive</i>	<i>Compounds that would give a positive result</i>
I ₂ /NaOH(aq)
Na ₂ CO ₃ (aq)
FeCl ₃ (aq)

- (d) Compound **W** can be oxidised to produce benzene-1,4-dioic acid (*terephthalic acid*). This reaction can be undertaken in the same way as the oxidation of methylbenzene to form benzenecarboxylic acid.



- (i) Give the reagent(s) and condition(s) required for this oxidation reaction. [2]

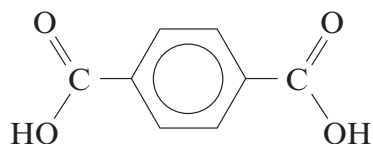
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- (ii) Almost all the benzene-1,4-dioic acid produced worldwide is used in the production of condensation polymers.

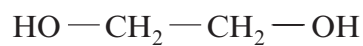
- I. Give **two** differences between condensation polymerisation and addition polymerisation. [2]

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- II. Draw the repeat unit for the polymer formed between benzene-1,4-dioic acid and ethane-1,2-diol. [1]

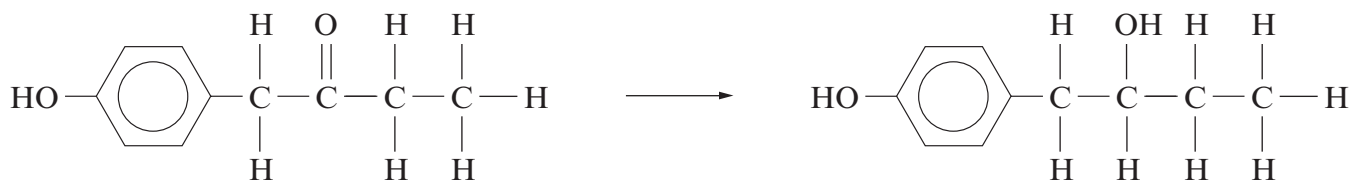


benzene-1,4-dioic acid
(*terephthalic acid*)



ethane-1,2-diol

- (e) Compound **Z** may be converted into a secondary alcohol as shown below.



compound **Z**

compound **V**

- (i) Give a suitable reagent for this process and classify the reaction that occurs. [2]

Reagent

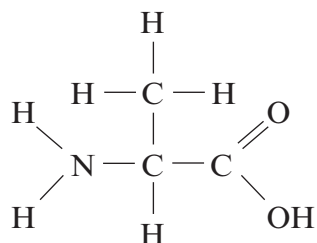
Classification of reaction

- (ii) Compound V will react with ethanoyl chloride.
Give the structure of a carbon-containing product of this reaction. [1]
- (iii) Compound V is insoluble in cold water, but reacts with sodium hydroxide solution and then dissolves.
Give the structure of the carbon-containing species present in the resulting solution. [1]

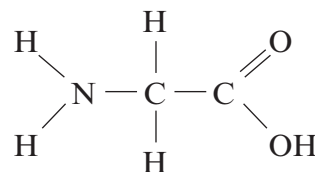
Total [19]

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

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

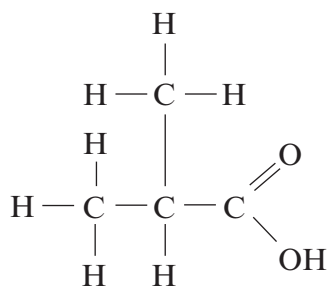


alanine
(2-aminopropanoic acid)



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]

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

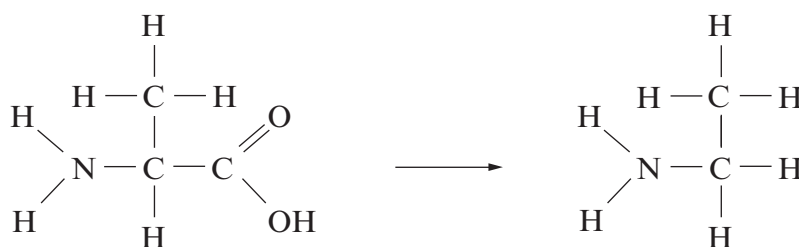
(iii) Circle the peptide linkage in **one** of your dipeptides. [1]

(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]

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



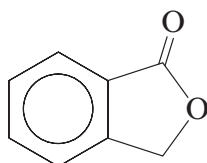
Name the reagent required for this reaction. [1]

Total [10]

3. Read the passage below and then answer the questions in the spaces provided.

Phthalides

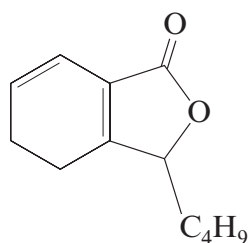
Phthalides are a family of compounds which are present in many plants, fungi and moulds. They are all based around the basic phthalide structure which has a benzene ring with a five-membered cyclic ester attached to it.



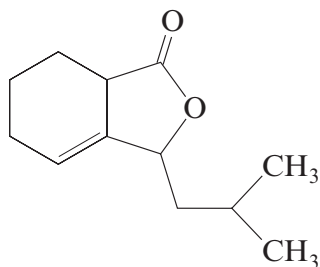
phthalide

- 5 Many phthalide-containing plants have been used worldwide as herbal remedies in traditional and folk medicines, and these have been found to affect many biological systems. 3-arylpthalides are also useful intermediates in the synthesis of anthracycline antibiotics.

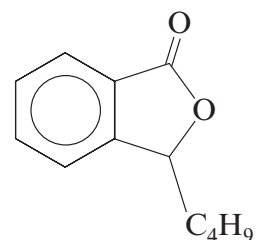
- 10 Some phthalides and their derivatives also act to enhance the flavour of food. In studies of celery, it was found that three particular compounds present in the plant had no flavour of their own, but enhanced the flavours of other foods when cooked together. These three were sedanenolide, sedanolide and 3-butylphthalide.



sedanenolide



sedanolide

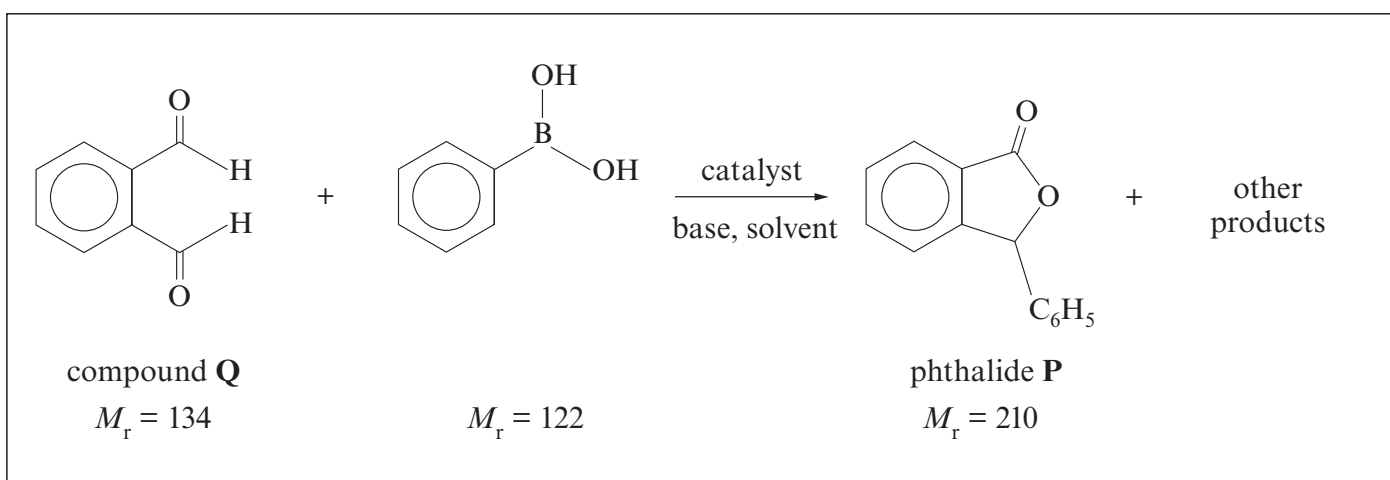


3-butylphthalide

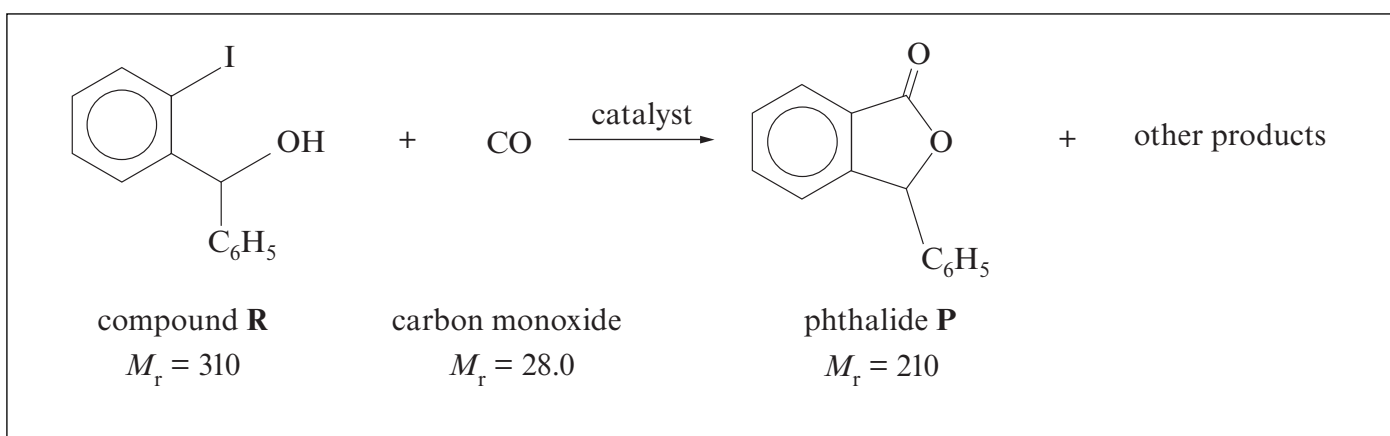
These molecules, amongst many others, are present in substantial amounts in oil of celery seed. These compounds are usually liquids with different boiling temperatures.

- 15 Due to the phthalide structure being a key part of useful molecules, there have been many attempts at synthetic routes to produce this structure. Two successful methods to form 3-phenylphthalide are shown as route 1 and route 2 opposite. Route 1 was developed more recently than route 2, and is considered to be a significant improvement. One reason for considering route 1 to be the better approach is the greater variety of different phthalides that can be produced by this method, whilst route 2 is only useful for a limited number of
- 20 phthalides.

Route 1



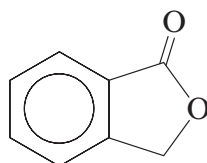
Route 2



– End of passage –

(a) Phthalides are considered to be cyclic esters (*line 3*).

(i) Indicate the ester group on the diagram of phthalide below by drawing a circle around it. [1]

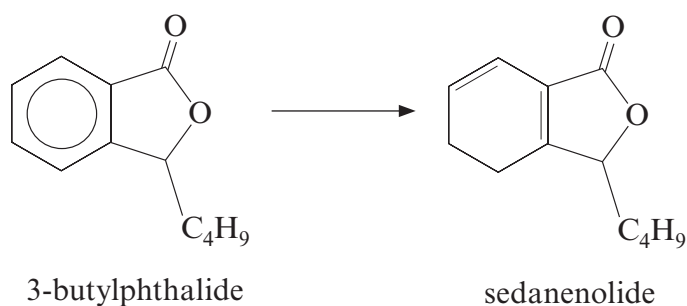


phthalide

(ii) Esters can be hydrolysed by heating with dilute sodium hydroxide solution. Draw the structure of the ion formed by hydrolysis of phthalide in this way. [1]

(b) Celery seed oil contains many different compounds (*lines 13-14*). Suggest a method for obtaining pure samples of each different compound. [1]

(c) It is possible to convert 3-butylphthalide into sedanenolide in a hydrogenation reaction.



In this case the enthalpy change is $+20 \text{ kJ mol}^{-1}$. The enthalpy change during hydrogenation of an alkene to form an alkane is typically -120 kJ mol^{-1} . Explain this significant difference in enthalpy values for these two reactions. [2]

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- (d) The atom economy for route 1 to produce phthalide **P** is 82.0%.
Calculate the atom economy for route 2 to produce **P**.

[1]

- (e) Route 1 is considered to be the better of the two methods for producing phthalides
(*line 18*).

- (i) Give **one** reason stated in the passage for considering route 1 to be the better
method. [1]

- (ii) Give **one** reason not stated in the passage for considering route 1 to be the better
method. [1]

- (f) Give a chemical test that would distinguish between compound **Q** and compound
R (*page 9*). Include any reagent(s) required and state the observations expected for
each compound. [3]

Reagent(s)

Observations

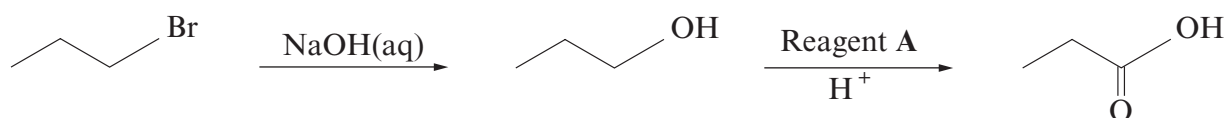
Total [11]

Total Section A [40]

SECTION B

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

4. (a) 1-bromopropane can be used to prepare propanoic acid in a two-stage process shown below.



- (i) Classify the reaction occurring in the first stage of this process. [1]
- (ii) The first stage uses aqueous sodium hydroxide. Under alternative conditions, 1-bromopropane produces a different product when it reacts with sodium hydroxide. Give the alternative conditions required, and the product that would be formed from 1-bromopropane under these conditions. [2]
- (iii) For the second stage, state the **full name** of reagent **A** and classify the reaction occurring. [2]
- (iv) Reagent **A** can also be used to produce propanal from propan-1-ol. State how you would isolate propanal from this reaction. [1]
- (b) (i) 1-bromopropane can also be used to prepare butanoic acid in a different two-stage process. For **each** of these two stages, give reagents and conditions required, and draw the **displayed** formula (showing all bonds) of the intermediate. [3]
- (ii) Butanoic acid is used to prepare esters used in the flavouring and perfume industries. It may be prepared from 1-bromopropane in a two-stage process as in (b)(i) above or from butan-1-ol or butanal in a one-stage process.
- Suggest **two** factors that a scientist would consider in choosing between these different routes to produce butanoic acid on a bulk scale. [2]
- (c) Compound **B** is an isomer of formula $C_4H_8O_2$ which exists as a sweet-smelling liquid at room temperature.
- (i) Elemental analysis of compound **B** shows that it has a composition of 54.5% carbon, 9.1% hydrogen and 36.4% oxygen, by mass. Show that this composition is consistent with the formula above. [2]

(ii) Compound **B** shows three resonances in its ^1H nuclear magnetic resonance spectrum.

- A triplet at 1.0 ppm with an area of 3
- A singlet at 2.1 ppm with an area of 3
- A quartet at 4.0 ppm with an area of 2

The infrared spectrum of compound **B** shows absorptions at 2981 cm^{-1} and 1750 cm^{-1} .

These are the only significant absorptions above 1500 cm^{-1} .

Using **all** the information supplied, deduce the structure of compound **B**.

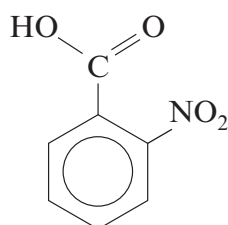
Give **reasons** in support of your answer.

[5]
(QWC) [2]

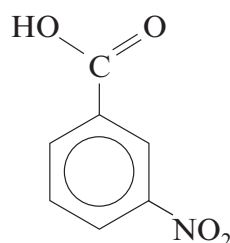
Total [20]

5. (a) Nitrobenzenecarboxylic acids (*nitrobenzoic acids*) are useful starting materials in the preparation of many dyes and can be prepared by nitration of benzenecarboxylic acid (*benzoic acid*), C_6H_5COOH .

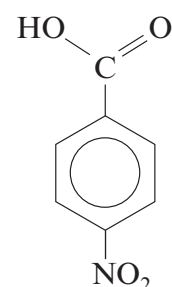
Many nitrobenzoic acids exist including those shown below:



2-nitrobenzoic acid

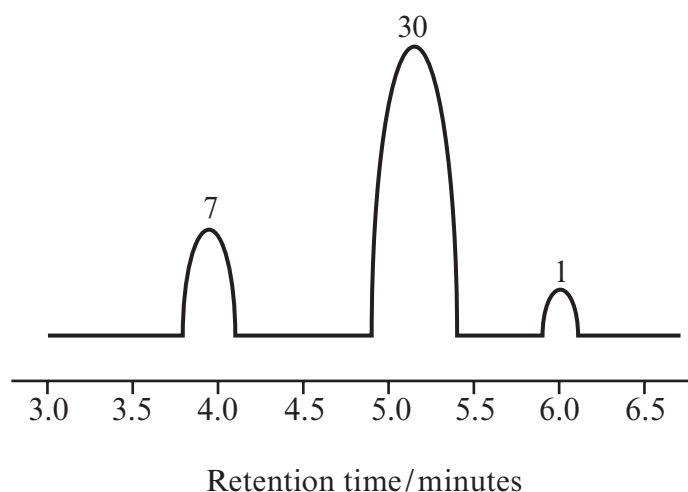


3-nitrobenzoic acid



4-nitrobenzoic acid

- (i) Benzenecarboxylic acid can be nitrated under similar conditions to the nitration of benzene.
Give the reagent(s) and condition(s) required and classify the mechanism of this reaction. [3]
- (ii) Nitration of benzenecarboxylic acid gives a mixture of products. These can be identified by gas chromatography followed by mass spectrometry (*GC-MS*). The gas chromatograph for the products of this reaction is shown below, with the relative areas of each peak indicated.



- I. The main isomer produced is 3-nitrobenzenecarboxylic acid.
Calculate the percentage of this isomer produced. [2]
- II. The mass spectrum of 3-nitrobenzenecarboxylic acid has main peaks at m/z 45, 46, 122 and 167. Suggest which species are responsible for **each** of these peaks. [2]

(iii) An impure sample of 3-nitrobenzenecarboxylic acid was obtained.

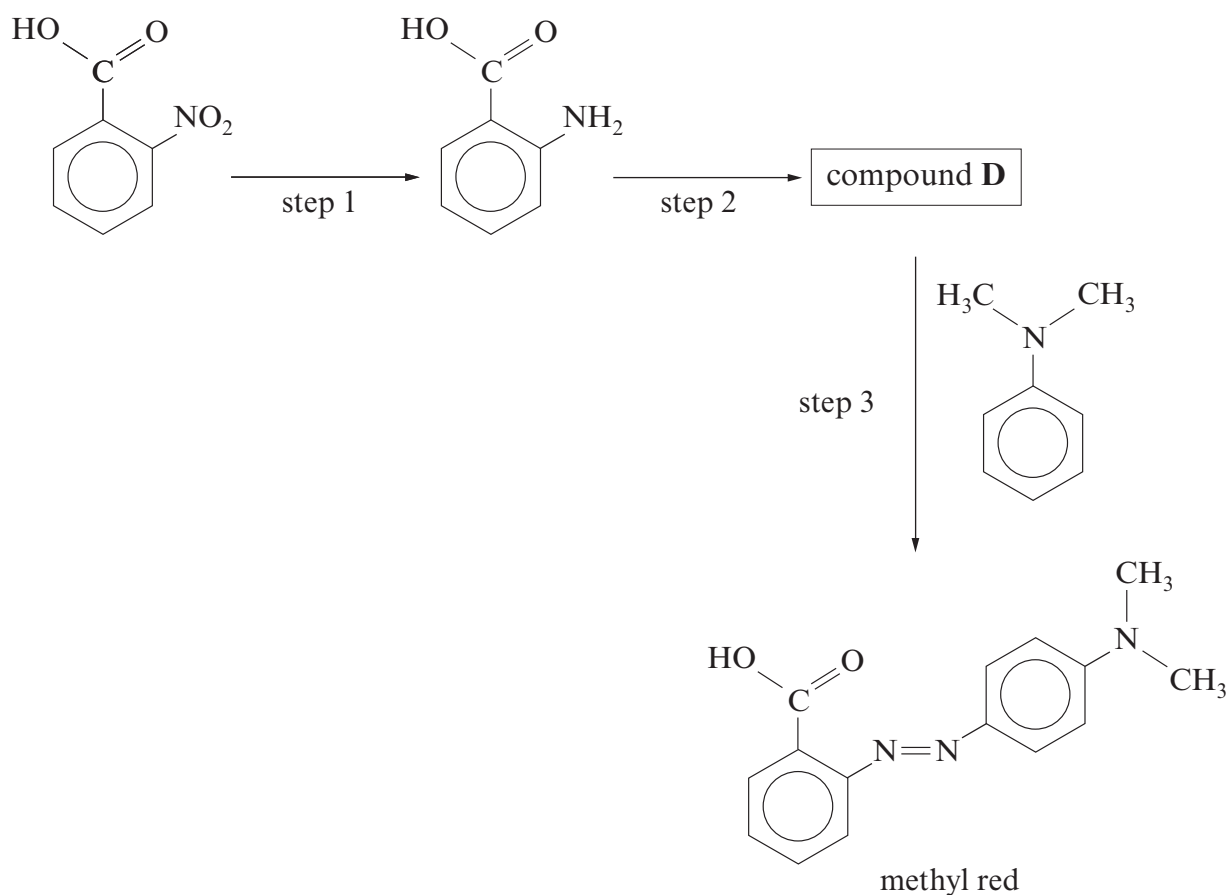
- I. State how the melting temperature of the impure sample of 3-nitrobenzenecarboxylic acid would differ from that of pure 3-nitrobenzenecarboxylic acid, if at all. [1]
- II. 3-nitrobenzenecarboxylic acid was found to be soluble in boiling water but not in cold water. It has a melting temperature of 142 °C.

Describe how impure 3-nitrobenzenecarboxylic acid could be purified by recrystallisation. Include full experimental details. [4]

(QWC) [1]

QUESTION 5 CONTINUES ON PAGE 16

- (b) 2-nitrobenzenecarboxylic acid may be used as a starting material for the production of the indicator methyl red. A reaction scheme for this process is given below.



- (i) Give the reagent(s) necessary for step 1. [1]
- (ii) Step 2 uses a mixture of sodium nitrate(III), NaNO_2 , with dilute hydrochloric acid. Give the conditions required for this reaction and the structure of the product, compound **D**. [2]
- (iii) Methyl red is red below pH 4. Explain the origin of this colour. [2]
- (c) Methyl red is used to differentiate between acids and bases. Explain why amines such as ethylamine are bases. [2]

Total [20]

Total Section B [40]



GCE A level

1094/01-A

**CHEMISTRY – DATA SHEET
FOR USE WITH CH4**

A.M. WEDNESDAY, 13 June 2012

Infrared Spectroscopy characteristic absorption values

Bond	Wavenumber/cm ⁻¹
C—Br	500 to 600
C—Cl	650 to 800
C—O	1000 to 1300
C=C	1620 to 1670
C=O	1650 to 1750
C≡N	2100 to 2250
C—H	2800 to 3100
O—H	2500 to 3550
N—H	3300 to 3500

Nuclear Magnetic Resonance Spectroscopy

Candidates are reminded that the splitting of any resonance into **n** components indicates the presence of **n-1** hydrogen atoms on the **adjacent** carbon, oxygen or nitrogen atoms.

Typical proton chemical shift values (δ) relative to TMS = 0

Type of proton	Chemical shift (ppm)
—CH ₃	0.1 to 2.0
R—CH ₃	0.9
R—CH ₂ —R	1.3
CH ₃ —C≡N	2.0
CH ₃ —C(=O)	2.0 to 2.5
—CH ₂ —C(=O)	2.0 to 3.0
—O—CH ₃ , —OCH ₂ —R, —O—CH=C	3.5 to 4.0
R—OH	4.5 *
CH ₂ =C	4.8
R—C(=O)H	9.8 *
R—C(=O)OH	11.0 *

*variable figure dependent on concentration and solvent

THE PERIODIC TABLE

Group 1 2 3 4 5 6 7 0

Period 1 2 3 4 5 6 7

1	1.01 H Hydrogen 1	4.00 He Helium 2																	
2	6.94 Li Lithium 3	9.01 Be Beryllium 4	10.8 B Boron 5	12.0 C Carbon 6	14.0 N Nitrogen 7	16.0 O Oxygen 8	19.0 F Fluorine 9	20.2 Ne Neon 10											
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12	27.0 Al Aluminium 13	28.1 Si Silicon 14	31.0 P Phosphorus 15	32.1 S Sulfur 16	35.5 Cl Chlorine 17	40.0 Ar Argon 18											
4	39.1 K Potassium 19	40.1 Ca Calcium 20	45.0 Sc Scandium 21	47.9 Ti Titanium 22	50.9 V Vanadium 23	52.0 Cr Chromium 24	54.9 Mn Manganese 25	55.8 Fe Iron 26	58.7 Ni Nickel 28	58.9 Co Cobalt 27	63.5 Cu Copper 29	65.4 Zn Zinc 30	69.7 Ga Gallium 31	72.6 Ge Germanium 32	74.9 As Arsenic 33	79.0 Se Selenium 34	79.9 Br Bromine 35	83.8 Kr Krypton 36	
5	85.5 Rb Rubidium 37	87.6 Sr Strontium 38	88.9 Y Yttrium 39	91.2 Zr Zirconium 40	92.9 Nb Niobium 41	95.9 Mo Molybdenum 42	98.9 Tc Technetium 43	101 Ru Ruthenium 44	106 Pd Palladium 46	103 Rh Rhodium 45	108 Ag Silver 47	112 Cd Cadmium 48	115 In Indium 49	119 Sn Tin 50	122 Sb Antimony 51	128 Te Tellurium 52	127 I Iodine 53	131 Xe Xenon 54	
6	133 Cs Caesium 55	137 Ba Barium 56	139 La Lanthanum 57	179 Hf Hafnium 72	181 Ta Tantalum 73	184 W Tungsten 74	186 Re Rhenium 75	190 Os Osmium 76	195 Pt Platinum 78	192 Ir Iridium 77	197 Au Gold 79	201 Hg Mercury 80	204 Tl Thallium 81	207 Pb Lead 82	209 Bi Bismuth 83	(210) Po Polonium 84	(210) At Astatine 85	(222) Rn Radon 86	
7	(223) Fr Francium 87	(226) Ra Radium 88	(227) Ac Actinium 89																

Key

A_r	relative atomic mass
Symbol	atomic number
Name	
Z	

d Block

f Block

140 Ce Cerium 58	141 Pr Praseodymium 59	144 Nd Neodymium 60	(147) Pm Promethium 61	150 Sm Samarium 62	(153) Eu Europium 63	157 Gd Gadolinium 64	159 Tb Terbium 65	163 Dy Dysprosium 66	165 Ho Holmium 67	167 Er Erbium 68	169 Tm Thulium 69	173 Yb Ytterbium 70	175 Lu Lutetium 71
232 Th Thorium 90	(231) Pa Protactinium 91	238 U Uranium 92	(237) Np Neptunium 93	(242) Pu Plutonium 94	(243) Am Americium 95	(247) Cm Curium 96	(245) Bk Berkelium 97	(251) Cf Californium 98	(254) Es Einsteinium 99	(253) Fm Fermium 100	(256) Md Mendelevium 101	(254) No Nobelium 102	(257) Lr Lawrencium 103

► Lanthanoid elements

►► Actinoid elements