

Surname	Centre Number	Candidate Number
Other Names		2



GCE A level

1094/01

CHEMISTRY CH4

P.M. WEDNESDAY, 15 June 2011

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.

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SECTION A

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

1. (a) Nitrobenzene, $C_6H_5NO_2$, is a yellow oily liquid.

(i) Give the general name of a group responsible for colour in organic compounds. [1]

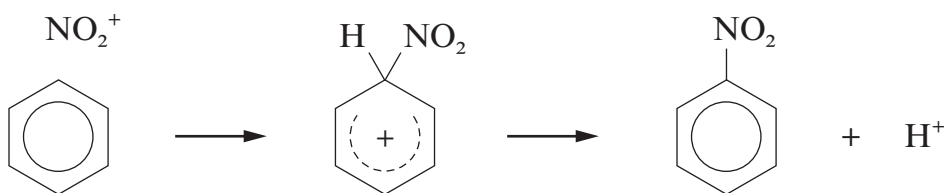
.....

(ii) State why nitrobenzene is yellow in white light. [1]

.....

(b) Nitrobenzene is produced from benzene by reaction with the nitronium ion (nitryl cation), NO_2^+ .

(i) Complete the mechanism below by the use of the curly arrows (\curvearrowright) [1]



(ii) During this reaction to produce nitrobenzene small quantities of 1,3-dinitrobenzene are produced.
Give the **empirical** formula of 1,3-dinitrobenzene. [1]

.....

(iii) In this reaction the nitronium ion is produced from nitric and sulfuric acids.



Use this equation to state why the sulfuric acid is acting as an acid. [1]

.....

.....

- (c) Explain why benzene compounds tend to react by electrophilic **substitution** rather than undergo electrophilic addition. [2]

(QWC) [1]

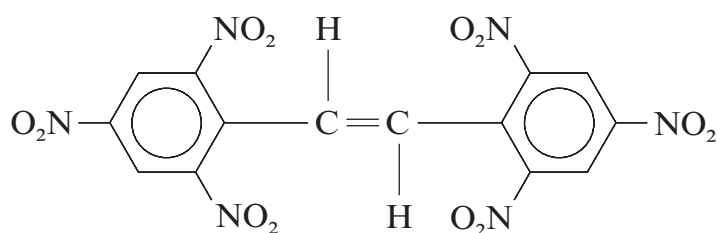
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- (d) Many explosives contain nitro-groups. The explosive hexanitrostilbene (HNS)



hexanitrostilbene

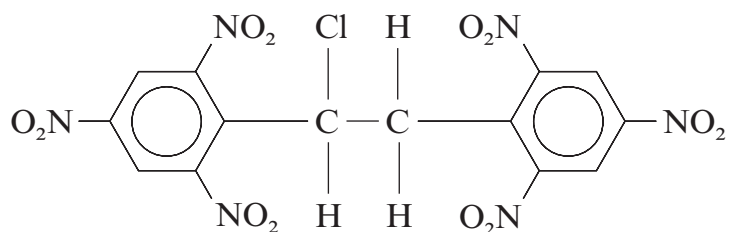
has been used to separate different sections in space rockets and for seismic experiments on the Moon.

- (i) HNS is the E-isomer of a pair of E-Z isomers. State why HNS has both E- and Z-isomers. [1]

.....

.....

- (ii) The manufacture of HNS is believed to proceed via compound **R**.



compound **R**

- I Compound **R** contains a chiral centre. Identify the chiral centre in the formula of compound **R** by using an asterisk (*). [1]

- II Compound **R** exists as two enantiomers. Explain what is meant by the term *enantiomers* and how these affect plane-polarised light. [2]

.....

.....

.....

- III State the type of reaction that occurs when compound **R** is converted to HNS by the use of a suitable base. [1]

.....

Total [13]

2. (a) Butan-1-ol can be produced by the reduction of butanal.

(i) State the name of a reducing agent that can be used for this reaction. [1]

.....

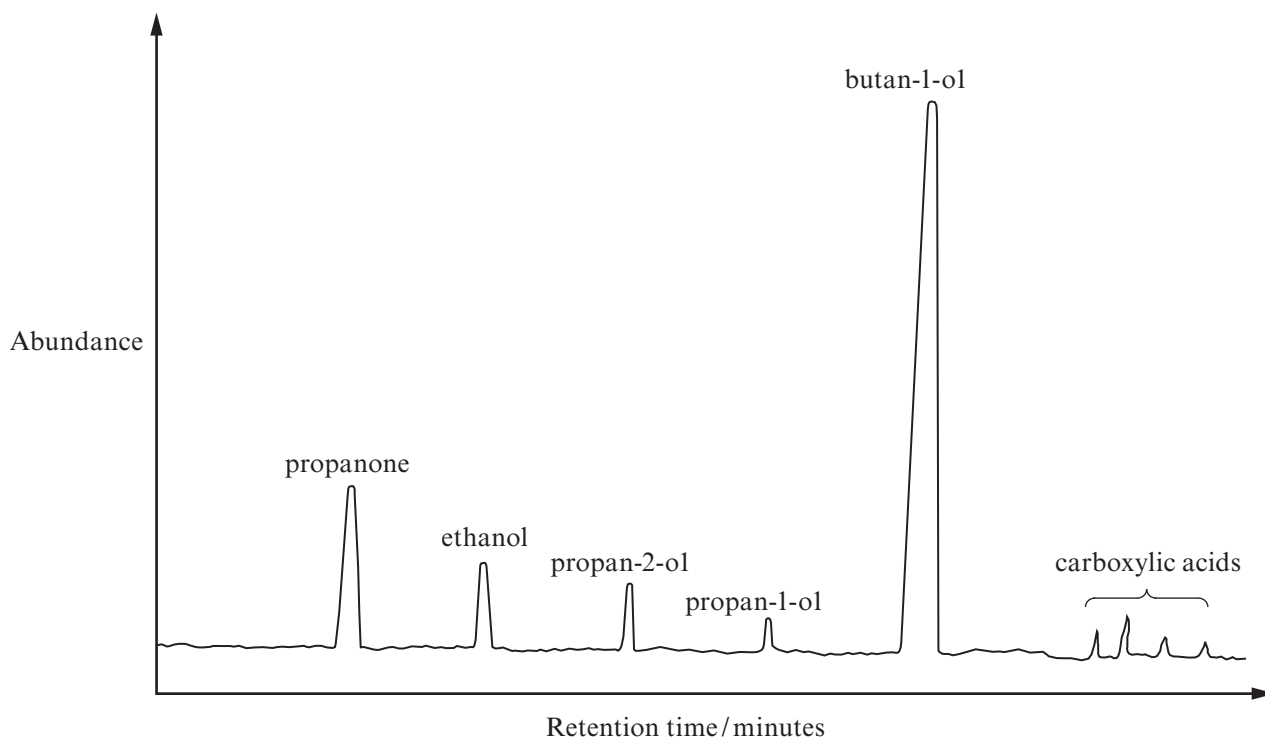
(ii) The infrared spectrum of butanal shows an absorption at 1731 cm^{-1} . State which bond in butanal is responsible for this absorption and explain how the intensity of this absorption changes as the reduction proceeds. [2]

.....

.....

.....

(b) A traditional route for making butan-1-ol is by the fermentation of sugar cane residues and other starch-containing materials. One problem with this method is that a number of other products are also obtained. The gas chromatogram shows the major products from a typical fermentation of starch.



Use the chromatogram to help you answer the questions below and opposite.

(i) State, in **decreasing** order of abundance, the three main products of this fermentation. [1]

.....

- (ii) State which **one** of the products in (i) **cannot** normally be oxidised to a carboxylic acid. [1]

.....

- (iii) Select **two** compounds, from the chromatogram, that will give a positive result in the triiodomethane (iodoform) reaction giving an explanation for your answer. [2]

Compounds and

Explanation

.....

.....

- (iv) Since there is a plentiful supply of cellulose from plants, scientists are using a new bacterium to ferment cellulose rather than starch. The first results of this research have been promising.
If this new method is to be tested by other research groups why is it essential that the conditions are kept exactly the same? [1]

.....

- (c) There is interest in developing butan-1-ol as a fuel to replace petrol and diesel as this would be a carbon neutral fuel.
Suggest why this fuel is described as carbon neutral, giving a reason for your answer. [2]

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.....

.....

- (d) A large proportion of the butan-1-ol produced is used to react with ethanoic acid to produce 1-butyl ethanoate.

- (i) Give the equation for this reaction. [1]

.....

- (ii) State the name of the catalyst that is used. [1]

.....

Total [12]

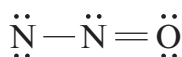
Read the passage below and then answer parts (a)-(g) in the spaces provided.

3.

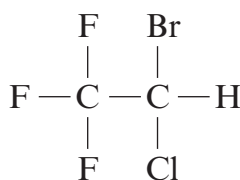
Anaesthetics

It is difficult to believe, in these days of modern medicine, that only 100 years ago tooth extractions were still being carried out without any form of anaesthetic. Modern anaesthetics are of two types – general anaesthetics, which have a whole body effect and local anaesthetics, which remove pain at the site of surgery.

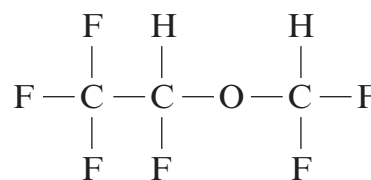
- 5 The first demonstrations of anaesthesia were in the late 1840s when Morton, in the USA, used ethoxyethane, and Simpson, in Scotland, used chloroform (trichloromethane). Later that century nitrous oxide, N_2O , was successfully used. In more recent times, up to about 1960, the most commonly used anaesthetics were cyclopropane and ethoxyethane. In the 21st century a number of safer general anaesthetics are in use, the choice depending on the condition for which they are being used. The formulae of some general anaesthetics are shown below, together with their common names.



nitrous oxide



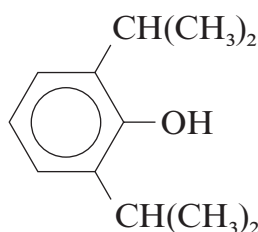
halothane



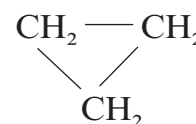
desflurane



ethoxyethane

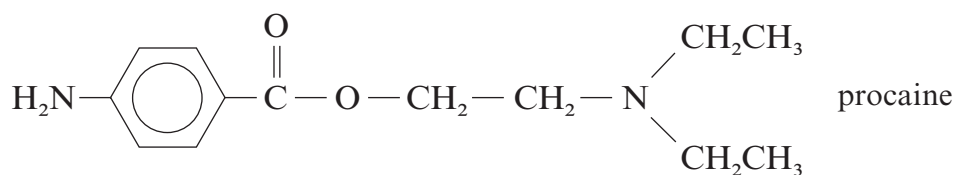


propofol



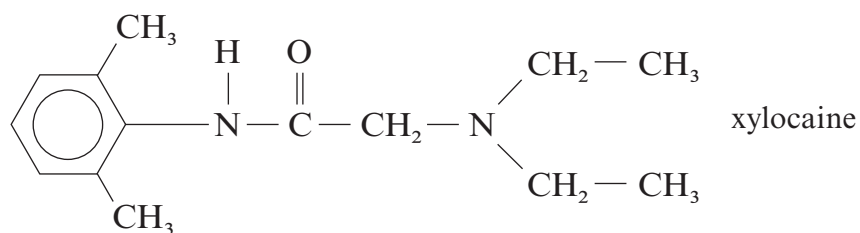
cyclopropane

- 15 In the twentieth century, the general anaesthetic nitrous oxide was still being used for routine dental extractions but in recent years the use of local anaesthetics has become the norm. A popular choice for dentists is the ester procaine, although a number of other compounds are available; their use depending on the anaesthetic effect required and its duration of action. The formulae and common names of some local anaesthetics are shown below.

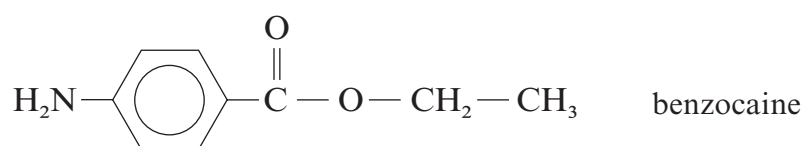


procaine

20



Benzocaine, for external use only, has uses in skin creams for which a numbing action is required.



25 The relative safety of the anaesthetic itself is an important factor in deciding which anaesthetic to use for each situation. However, another factor to be considered is the method by which the body metabolises the anaesthetic and the nature of the compounds that are produced.

– End of passage –

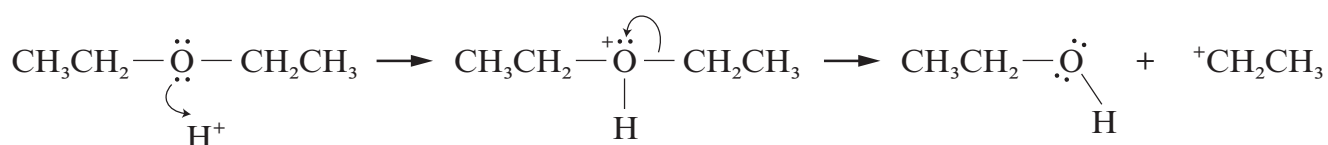
- (a) In the upper atmosphere nitrous oxide (dinitrogen oxide), N_2O , decomposes to nitrogen and nitrogen monoxide.



Nitrogen monoxide is a reactive molecule that contains an unpaired electron. State the general name for species that contain an unpaired electron. [1]

- (b) The use of cyclopropane as an anaesthetic causes concern because of its extreme flammability. Give the balanced equation for the complete combustion of cyclopropane, C_3H_6 . [1]

- (c) Ethoxyethane, $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, reacts with some aqueous acids to give ethanol as one of the products. One stage of this reaction can be represented as follows:



- (i) State why ethoxyethane is behaving as a nucleophile in this reaction stage. [1]

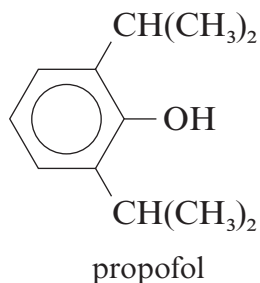
- (ii) I To reduce the danger of fire when carrying out this reaction, the reactants are heated together under reflux. State what is meant by the term *heating under reflux*. [1]

- II The reactants need to be refluxed at a temperature of 130°C . Suggest how this mixture could be safely heated at this temperature in a laboratory fume cupboard. [1]

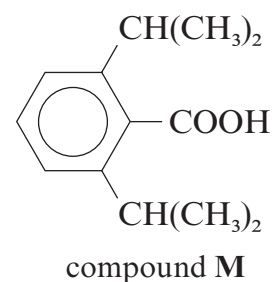
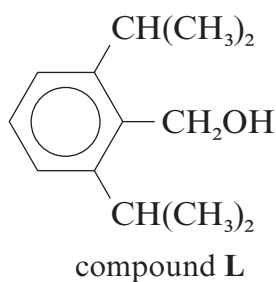
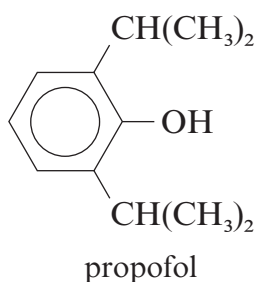
- (d) The article mentions the use of halothane (*line 12*) and desflurane (*line 12*) as general anaesthetics. State and explain which of these two compounds could cause more damage to the ozone layer. [2]

(e) Propofol, which allegedly caused the death of Michael Jackson in 2009, is an important intravenous anaesthetic.

(i) State what would be seen if a few drops of iron(III) chloride solution were added to a solution of propofol in a suitable solvent. [1]



(ii) The formulae of propofol, compound **L** and compound **M** are shown below.



I The three compounds are dissolved separately in a suitable solvent and each solution tested with universal indicator paper and with sodium hydrogencarbonate solution. Complete the table below giving any **observations** or writing 'no reaction' as appropriate.

Compound	Colour given with universal indicator paper	Observation with sodium hydrogencarbonate solution
propofol		
compound L	green	no reaction
compound M		

[2]

II Give the test for any gas produced with sodium hydrogencarbonate solution. [1]

- (f) The article describes procaine (*line 19*) as an ester.
- (i) Draw the section of the formula that identifies procaine as an ester. [1]
- (ii) Use the formula of procaine to help you draw the structural formula of the nitrogen-containing alcohol that will react with a suitable acid to give procaine. [1]
- (g) Pure benzocaine has a melting temperature of 89°C. A melting temperature determination shows that a sample of benzocaine is impure. State **two** observations that would indicate that this sample is impure. [2]

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Total [15]

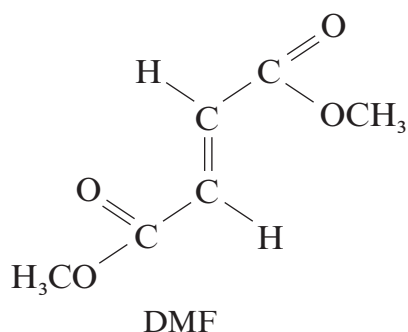
Total Section A [40]

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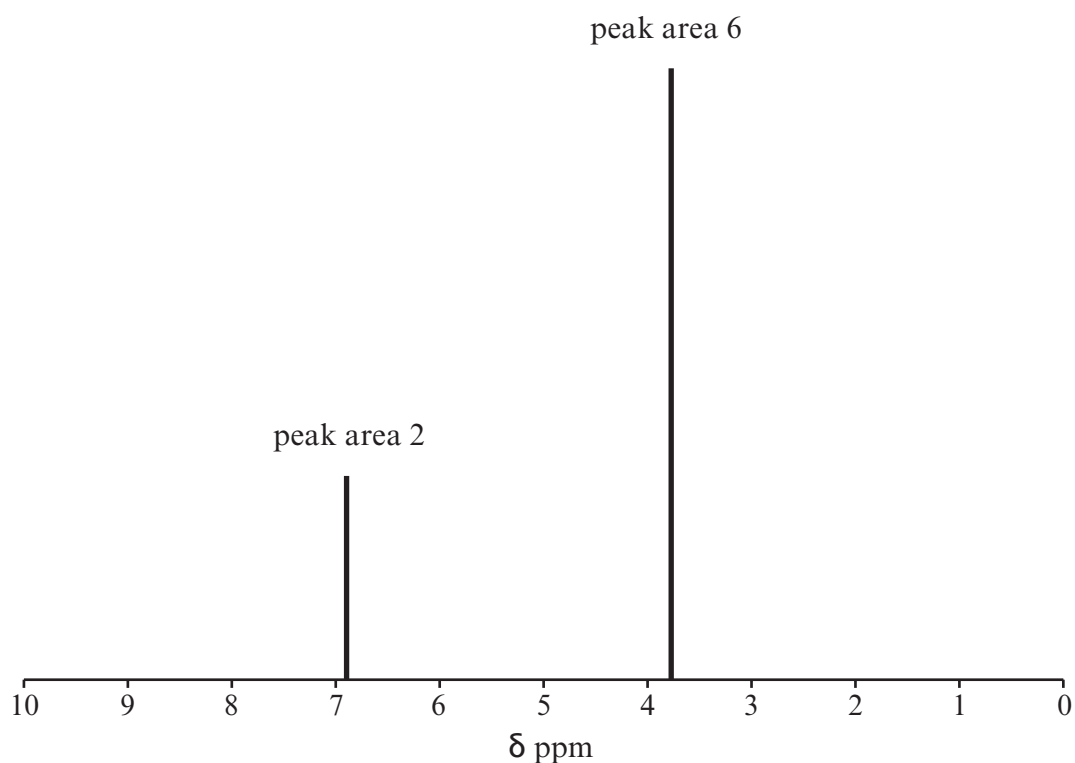
SECTION B

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

4. (a) In 2009 a man received compensation after he received chemical burns from a compound used as an antifungal agent in an imported leather sofa. The compound causing this problem was the ester dimethyl fumarate (DMF).



- (i) DMF is one of a pair of E-Z stereoisomers. State what is meant by *stereoisomerism* and draw the displayed formula of the other stereoisomer of DMF. [2]
- (ii) The NMR spectrum of the ester DMF is shown below.



The hydrolysis of dimethyl fumarate produces the dicarboxylic acid, fumaric acid. Describe how the NMR spectrum of fumaric acid would be different from the NMR spectrum of dimethyl fumarate.

Your answer should identify the peaks involved and include reasons for any changes that occur. You should also identify any NMR signal that does not change and the reasons for this. [5]

(QWC) [1]

(iii) The mass spectrum of DMF, $C_6H_8O_4$, shows only a weak signal for its molecular ion at m/z 144. The strongest signal is seen at m/z 113. Suggest a molecular formula for the positive ion at m/z 113, giving your reasoning. [2]

(b) Fumaric acid (*E*-butenedioic acid) is an important starting compound for the manufacture of many other materials. The usual method for producing fumaric acid is from crude oil, but there is increasing interest in a fermentation route, using enzymes, from a sugar such as glucose. A comparison of these two methods is shown in the table.

	Crude oil route	Fermentation route
Raw material	Maleic anhydride	Glucose
Reaction temperature / °C	95	35
Raw material price / £ kg ⁻¹	1.00	0.30

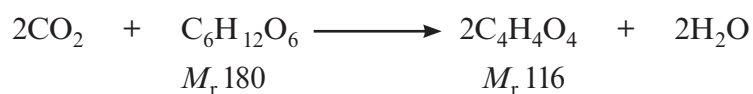
(i) Suggest **one** way that the crude oil route could be made more economic to operate. [1]

(ii) At present the crude oil route is the more economic route from which to obtain fumaric acid.

Suggest **one** factor by which the fermentation route could be modified to make it more competitive with the crude oil route, other than by simply increasing the yield. You are reminded that the optimum temperature for enzymes in this reaction is 35°C. [1]

(iii) Fumaric acid was obtained in a pilot-scale experiment by the fermentation route, using glucose.

A simplified equation for the reaction is shown below.



In this experiment 12.6 kg of glucose (70 moles) gave 13.0 kg of fumaric acid. Calculate the percentage yield of fumaric acid. [3]

(iv) Small amounts of other organic acids are produced during the fermentation.

I One of these acids is ethanoic acid.

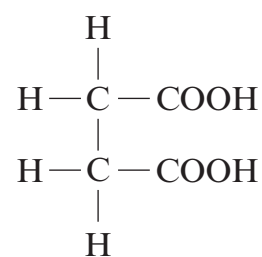
Outline any **one** other reaction that produces ethanoic acid.

Your answer should include

- the name of your starting material,
- any other reagent(s) used,
- the type of reaction occurring.

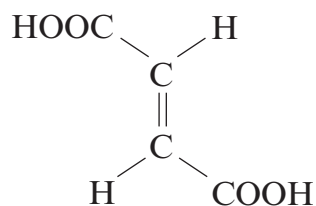
[3]

II A small amount of butanedioic acid is also produced.



butanedioic acid

This acid can also be produced by the hydrogenation of the unsaturated acid, fumaric acid.

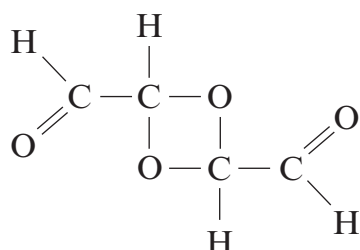


fumaric acid

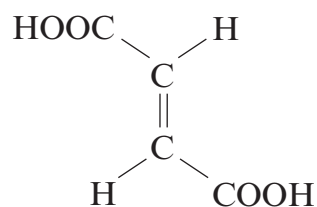
Suggest a suitable catalyst for this hydrogenation.

[1]

(c) A research student claimed to have made compound **U**, which is an isomer of fumaric acid.



compound **U**



fumaric acid

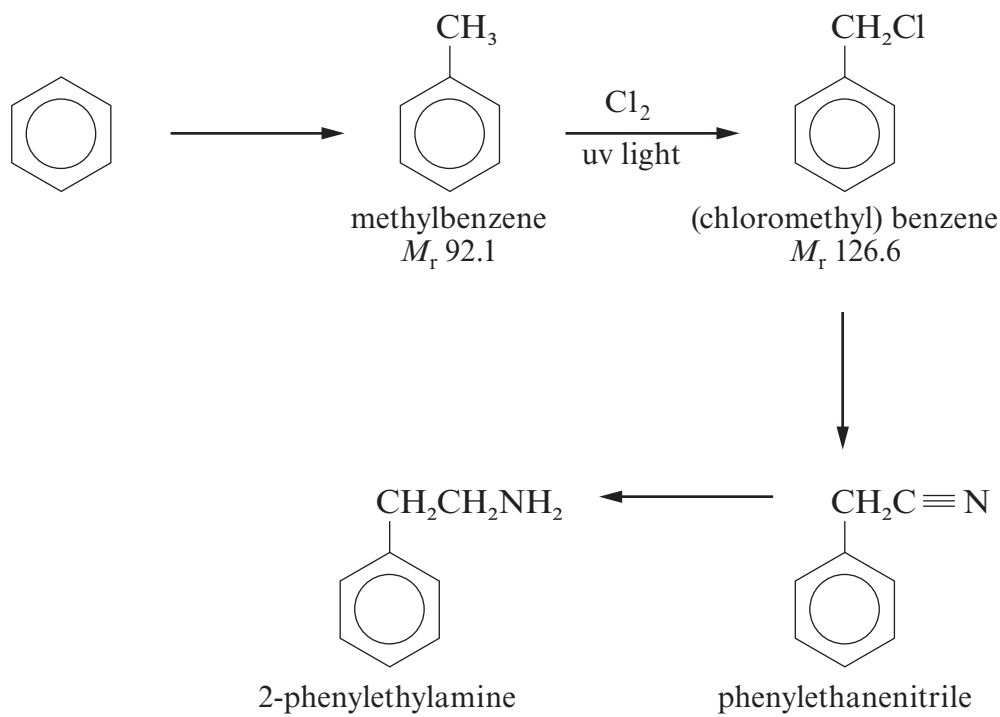
State a reagent that would react with compound **U** and **not** fumaric acid, giving the result of the test.

[1]

Total [20]

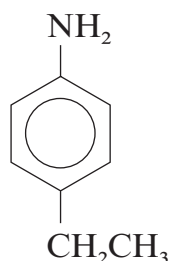
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5. (a) 2-Phenylethylamine, present in chocolate, can be made from benzene in four stages.



- (i) Give the equation, and the name of a suitable catalyst, for the Friedel-Crafts alkylation of benzene leading to methylbenzene. [2]
- (ii) (Chloromethyl)benzene is produced by passing chlorine gas into methylbenzene in the presence of ultraviolet light. In practice the substitution by chlorine can proceed further giving (dichloromethyl)benzene and (trichloromethyl)benzene. In order to prevent further chlorination the reaction is stopped when the increase in mass corresponds to (chloromethyl)benzene being produced. You should assume that the other product, gaseous hydrogen chloride, is lost from the mixture. In an experiment the following results were obtained.
- | | | | | |
|---------------|---|---------------|---|---------|
| Mass of flask | + | product | = | 158.4 g |
| Mass of flask | + | methylbenzene | = | 148.0 g |
| Mass of flask | | | = | 120.4 g |
- Show that the increase in mass corresponds to the conversion of all the methylbenzene into (chloromethyl)benzene. [4]
- (iii) State the names of the reagents necessary to convert
- I (chloromethyl)benzene to phenylethanenitrile, [1]
- II phenylethanenitrile to 2-phenylethylamine. [1]

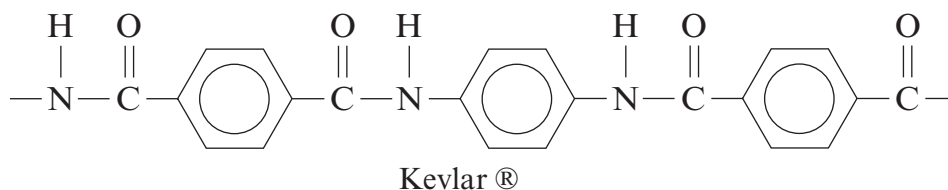
- (b) Explain why 2-phenylethylamine is a base. [2]
- (c) State how both 2-phenylethylamine and its isomer 4-ethylphenylamine react with nitric(III) (nitrous) acid at 5°C.



4-ethylphenylamine

In **each** case you should state the type of compound produced and any relevant observations. [3]

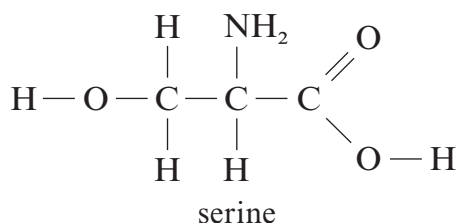
- (d) Kevlar® is a polyamide that is used in bullet-proof vests.



Kevlar®

Give the formula of two starting materials that can be reacted together to give Kevlar®. [2]

- (e) Silk is a naturally occurring material composed of polymerised serine molecules. Serine is an α -amino acid.



serine

- (i) Give the **systematic name** of serine, which is a derivative of propanoic acid. [1]
- (ii) Hydrogen bonding is largely responsible for the solubility of serine in water. Explain what is meant by hydrogen bonding, using serine to illustrate your answer. [3]

(QWC) [1]

Total [20]

Section B Total [40]



GCE A level

1094/01-A

**CHEMISTRY CH4
DATA SHEET**

P.M. WEDNESDAY, 15 June 2011

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	s Block		d Block										p Block		f Block					
1	1.01 H Hydrogen 1																4.00 He Helium 2			
2	6.94 Li Lithium 3	9.01 Be Beryllium 4															19.0 F Fluorine 9	20.2 Ne Neon 10		
3	23.0 Na Sodium 11	24.3 Mg Magnesium 12															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	58.9 Co Cobalt 27	58.7 Ni Nickel 28	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	103 Rh Rhodium 45	106 Pd Palladium 46	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	192 Ir Iridium 77	195 Pt Platinum 78	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																	
			▶ Lanthanoid elements	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			
		▶ Actinoid elements	232 Th Thorium 90	(231) Pa Protactinium 91	238 U Uranium 92	(237) Np Neptunium 93	(242) Pu Plutonium 94	(243) Am Americium 95	(245) Bk Berkelium 97	(247) Cm Curium 96	(251) Cf Californium 98	(254) Es Einsteinium 99	(254) Fm Fermium 100	(253) Md Mendelevium 101	(256) No Nobelium 102	(254) Lr Lawrencium 103				

Key

A_r	relative atomic mass
Symbol	Name
Z	atomic number