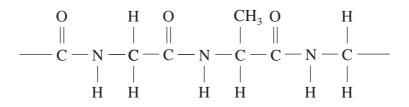
(ii) Draw the displayed formula of the zwitterion structure of aminoethanoic acid. [1]

(*d*) The formula of a section of a polypeptide is given below.



This formula represents the primary structure of a protein.

Briefly outline how the **secondary** structure of a protein arises from the primary structure.

[2]

(QWC) [1]

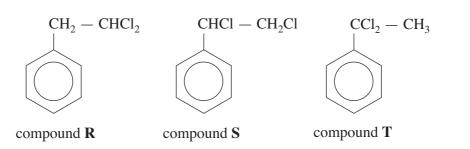
Total [12]

Examiner only

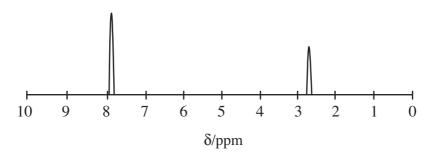
Turn over.

Examiner only

(b) (2-Chloroethyl)benzene can be made by reacting ethylbenzene with chlorine. During this reaction a number of other compounds, including the following, are produced.

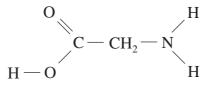


The low resolution NMR spectrum of one of these compounds is shown below.



State, giving a reason, which of the three compounds \mathbf{R} , \mathbf{S} or \mathbf{T} will have the low resolution NMR spectrum shown. [2]

(c) (i) Aminoethanoic acid (glycine), whose displayed formula is shown below, reacts with ethanoyl chloride.



Give the equation for this reaction, showing the displayed formula of the organic product. [2]

6

5.

- (a) (i) Give an equation for the preparation of butylamine from a halogenoalkane. [1]
 - (ii) Discuss how the presence of the $-NH_2$ group in butylamine results in butylamine having a higher boiling temperature than expected for a molecule of this size. [4]
 - (iii) An aqueous solution of butylamine was tested using pH indicator/paper.
 State the colour that was observed and **explain** why butylamine is able to cause this colour change.
 [3]
 - (b) Amides have important pharmacological and commercial uses and there is interest in the development of more economical production methods.
 - (i) In the past, the favoured method has been to heat the ammonium salts of carboxylic acids, for example ammonium butanoate gives butanamide.

$$CH_3CH_2CH_2COONH_4 \longrightarrow CH_3CH_2CH_2CONH_2 + H_2O$$

This is an energy-intensive process, which also gives small amounts of other products.

This makes the isolation of pure butanamide difficult.

In a pilot-scale experiment 50.0 kg of ammonium butanoate (M_r 105) was heated to produce 26.9 kg of butanamide (M_r 87).

Calculate the percentage yield of butanamide in this reaction. [3]

(ii) There is interest in developing processes that use less energy in production and separation, and that also give higher yields.In one new biochemical experiment, researchers used an enzyme from a suitable

In one new blochemical experiment, researchers used an enzyme from a suitable bacterium to convert butanenitrile to butanamide.

$$CH_{3}CH_{2}CH_{2}C \equiv N \longrightarrow CH_{3}CH_{2}CH_{2}C$$

Details of the method Temperature 10°C Time taken 6 hours Yield of butanamide > 99%

- I Before publishing their results the researchers repeated their experiment. State why this is an essential part of any research work. [1]
- II If you were a member of the research team that discovered this new reaction, suggest what should be the next stage of research before proceeding to a larger scale trial. [1]

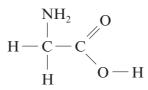
SECTION B

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



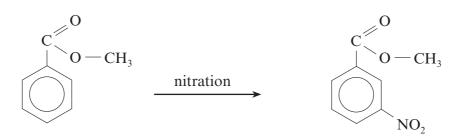
- (i) Draw the displayed formula of 2-aminopropanoic acid (alanine). [1]
- (ii) A dipeptide can be formed by reacting two amino acids. Draw the displayed formulae of the two different dipeptides which can be made by combining glycine and alanine.
- (iii) Proteins are natural polypeptides. Explain briefly what is meant by primary, secondary and tertiary protein structure. [3]

Total [20]

5. (a) Describe the structure of, and bonding in, benzene and explain why benzene is less ready to undergo addition reactions than alkenes. [6]

(QWC) [2]

(b) Frances wanted to prepare a nitro-aromatic compound in the laboratory, so her teacher told her to prepare methyl-3-nitrobenzoate by nitrating methyl benzoate using the following method.



methyl benzoate

methyl-3-nitrobenzoate

- Prepare a nitrating mixture by mixing 2 cm³ of concentrated nitric acid and 2 cm³ of concentrated sulfuric acid in a test tube, cooling it in ice.
- Weigh 2.75 g of methyl benzoate in a small conical flask, place the flask in a beaker of ice and slowly add 5 cm³ of concentrated sulfuric acid.
- Add the nitrating mixture a few drops at a time to the solution in the flask ensuring that the temperature stays below 10 °C.
- When the addition is complete, allow the mixture to stand at room temperature for 15 minutes.
- Pour the mixture onto crushed ice in a small beaker, stir and leave until all the ice has melted and crystals have formed.
- Filter the mixture, wash well with water and recrystallise it from ethanol.

At the end of the experiment Frances' yield was 2.70 g.

| (i) | Suggest why the teacher told her to nitrate methyl benzoate, not benzene. | | | | | |
|-------|---|-------------|--|--|--|--|
| (ii) | State why it is necessary to recrystallise the product before weighing it. | | | | | |
| (iii) | Outline how Frances would recrystallise methyl-3-nitrobenzoate from ethan | iol. [3] | | | | |
| (iv) | State how she could prove that the product was pure. | [1] | | | | |
| (v) | Methyl benzoate is a liquid at room temperature and has a density of 1.1 g cm Calculate the volume of 2.75 g of methyl benzoate. | | | | | |
| (vi) | Calculate the percentage yield obtained by Frances. | [3] | | | | |
| (vii) | Methyl benzoate undergoes nitration by the same mechanism as benzene. | | | | | |
| | I. Classify the mechanism for the nitration of methyl benzoate. | [1] | | | | |
| | II. Give the formula of the species attacking the benzene ring. | [1] | | | | |
| | | | | | | |

Total [20]

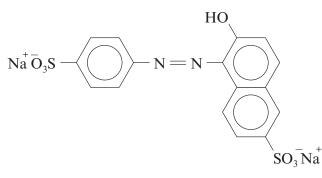
Section B Total [40]

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

Food additives

Since 1986 manufacturers have been required, for most foods, to list their ingredients in descending proportions by mass. Food additives can be listed by their chemical names or by using an E-number. They are used for a number of reasons and as a result they are classified into different groups, some of which are discussed in this article.

5 **Colouring agents** Consumers are probably most worried about compounds used to colour food. A number of permitted colours are synthetic azo-dyes and there are particular concerns about the effect that some of these compounds have on children. In recent years there has been a move towards safer naturally occurring dyes such as annatto and anthocyanins. However, azo-dyes such as Sunset Yellow FF (E110) continue to be used.



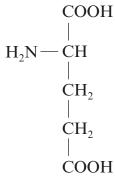
E110

- *10* **Preservatives** With the move towards foods having longer shelf lives, there is a need to use preservatives to prevent spoilage. 2-Hydroxypropanoic acid (lactic acid), occurs naturally in sour milk and is used as a preservative in salad dressings. The salts of organic acids, for example sodium benzoate and sodium citrate, are used in fizzy drinks.
- Calcium propanoate, $(CH_3CH_2COO)_2Ca$, is used as a preservative in bread, as it inhibits the 15 growth of mould-producing microorganisms.

Emulsifiers These are used to enable oily substances and water to mix, so that separation into two layers does not occur. These compounds generally have water-'soluble' groups and a hydrocarbon chain that is fat-'soluble'. An example is the ester E477.

E477

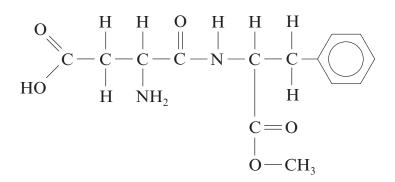
(e) MSG (*line 19*) is the monosodium salt of the α -amino acid glutamic acid.





Give the **structural** formula of the organic species produced when glutamic acid is dissolved in excess alkali. [1]

(f) The artificial sweetener aspartame is a common sweetener in soft drinks. However, these should not be kept for any length of time as the **ester group** slowly hydrolyses.



aspartame

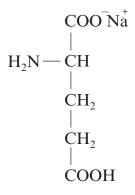
Give the structural formula of the two organic compounds produced from this hydrolysis of the ester group. [2]

Total [15]

Section A Total [40] Turn over.

icid.

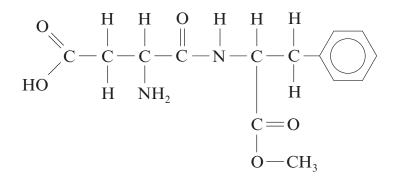
Examiner only **Flavour enhancers** Compounds such as monosodium glutamate (MSG) are added to food to increase its flavour. MSG occurs naturally in Parmesan cheese and tomatoes. Perhaps that is the reason why pizzas and soups are sometimes garnished with cheese and tomato.



MSG

Artificial sweeteners Many consumers are suspicious of food that has added sugar and manufacturers are naturally keen to label their products as containing 'no added sugar'. This may be true, but very often artificial sweetening agents are added in place of sugar to make
 25 the food more palatable. One of the commonest of these is aspartame, which is 200 times

25 the food more palatable. One of the commonest of these is aspartame, which is 200 sweeter than sugar.



aspartame

The use (and misuse) of additives is an area of chemistry that has increasing importance as world population increases leading to a greater reliance on prepared, rather than fresh food.

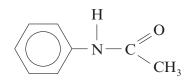
- End of passage -

14

SECTION B

Answer both questions in the separate answer book provided.

4. (a) Phenylamine reacts with ethanoyl chloride to produce N-phenylethanamide.

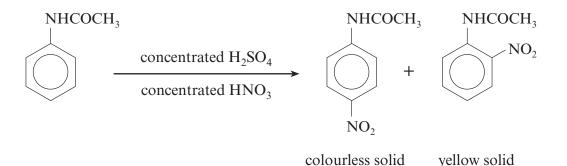


These two reactants are mixed together under suitable conditions and the products are poured into a large excess of cold water, when N-phenylethanamide is formed as impure white crystals. After filtering, N-phenylethanamide is recrystallised from hot water. The pure product melts at 113 °C.

- (i) Write the chemical equation for the reaction of phenylamine and ethanoyl chloride. [1]
- (ii) When filtering the mixture containing impure N-phenylethanamide, the material in the filter paper is washed several times with cold water.State why this is done. [1]
- (iii) Use the account above to help you describe how you would obtain pure, dry crystals of N-phenylethanamide from the impure white crystals. [4]

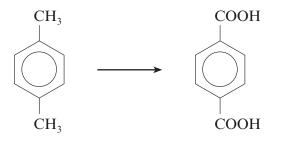
(QWC) [1]

(b) N-phenylethanamide can be nitrated using a mixture of concentrated nitric and sulfuric acids, giving mainly 4-nitro-N-phenylethanamide as colourless crystals, together with small quantities of the yellow 2-nitro-N-phenylethanamide.



 (i) The mechanism for this reaction is similar to the nitration of benzene. Give the reaction mechanism for the production of 4-nitro-N-phenylethanamide, starting from N-phenylethanamide and the nitronium ion (nitryl cation), NO₂⁺. Your answer should also state the type of reaction mechanism occurring. [4]

- (ii) The two isomers are separated by recrystallisation from ethanol, in which the 2-isomer is much more soluble.Use the information provided to state and explain how you would know when the 4-isomer is no longer contaminated with traces of the 2-isomer. [2]
- (iii) In an experiment 8.10 g of N-phenylethanamide (M_r 135) produced 6.48 g of pure 4-nitro-N-phenylethanamide (M_r 180). Calculate the percentage yield of 4-nitro-N-phenylethanamide. [3]
- (c) One stage in the preparation of the polyester PET is the oxidation of 1,4-dimethylbenzene to benzene-1,4-dioic acid.



This is carried out in the laboratory by refluxing 1,4-dimethylbenzene and an alkaline solution (containing sodium hydroxide) of an oxidising agent G, giving an intermediate product, which is then acidified.

- (i) State the name of oxidising agent **G**. [1]
- (ii) Explain why it is then necessary to acidify the intermediate product to give the required acid. [1]
- (d) The polyester PET is produced by reacting benzene-1,4-dioic acid and ethane-1,2-diol.
 Draw the formula of the repeating unit found in PET and state why this reaction is described as condensation polymerisation. [2]

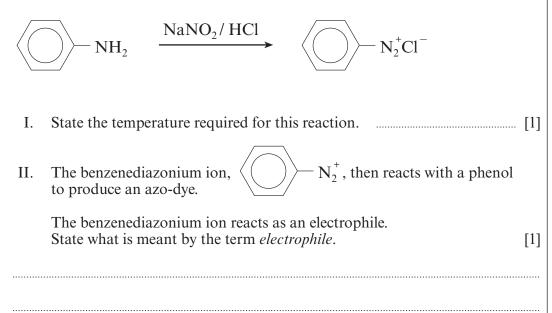
Total [20]

Examiner only



- (a) (i) State the general name given to groups present in compounds such as Sunset Yellow FF that gives them their colour. [1]
 - (ii) Sunset Yellow FF is soluble in water. Like sodium chloride it contains sodium ions, Na⁺. Explain how sodium ions interact with water molecules. [1]

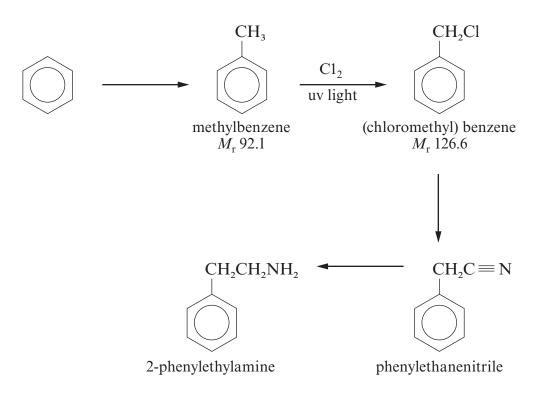
(iii) In the first stage of preparing an azo-dye, an aromatic amine reacts with sodium nitrate(III) (nitrite) and hydrochloric acid to give a diazonium compound.



only

- Examiner Explain why benzene compounds tend to react by electrophilic substitution rather than (c)undergo electrophilic addition. [2] (*QWC*) [1] (d)Many explosives contain nitro-groups. The explosive hexanitrostilbene (HNS) NO₂ O_2N Η NO₂ NO_2 Η O₂N hexanitrostilbene has been used to separate different sections in space rockets and for seismic experiments on the Moon. HNS is the E-isomer of a pair of E-Z isomers. State why HNS has both E- and (i) Z-isomers. [1] (ii) The manufacture of HNS is believed to proceed via compound **R**. NO₂ Cl Η O_2N NO_2 Η NO₂ Η O₂N compound **R**
 - Compound **R** contains a chiral centre. Identify the chiral centre in the formula Ι of compound **R** by using an asterisk (*). [1]

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.

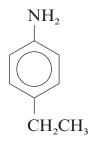
In an experiment the following results were obtained.

| 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]

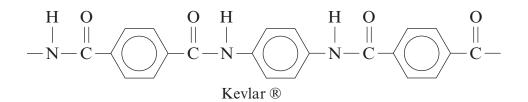
- (b) Explain why 2-phenylethylamine is a base.
- (c) State how both 2-phenylethylamine and its isomer 4-ethylphenylamine react with nitric(III) (nitrous) acid at 5°C.



4-ethylphenylamine

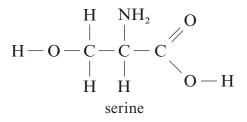
In each case you should state the type of compound produced and any relevant observations. [3]

(d) Kevlar \mathbb{R} is a polyamide that is used in bullet-proof vests.



Give the formula of two starting materials that can be reacted together to give Kevlar \mathbb{R} . [2]

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



- (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]

[2]

| | | | | | Exa | | | |
|--------|---|---------------------------------------|--|---|-------------|--|--|--|
| | | | SECTION A | | | | | |
| | | Answer a | all questions in the space. | s provided. | | | | |
|) [| The formulae of some compounds are shown below. | | | | | | | |
| | CH ₃ CH ₂ NH ₂ CH ₃ CH ₂ CONH ₂ CH ₃ CHCHCHO | | | | | | | |
| | | Α | В | С | | | | |
| (| CH ₃ | CH(OH)CH ₂ CH ₃ | CH ₂ CHCH ₃ | CH ₃ CH ₂ COCH ₂ CH ₃ | | | | |
| | | D | Ε | F | | | | |
| ł | belov | | | or not at all, to answer the ques | SUONS | | | |
| | (i) | is most basic, | | | [1] | | | |
| | (ii) forms yellow crystals when warmed with iodine in alkaline solution, [1] | | | | | | | |
| (1 | (iii) forms a silver mirror when warmed with Tollens' reagent, | | | | | | | |
| | (iv) | exhibits E-Z isomer | ism. | | [1] | | | |
|) | (i) | | f the compounds respon aboratory from 1-chlore | sible for the smell of rotting fish. | It can | | | |
| | | Classify the reaction | n mechanism when buty | lamine is prepared in this way. | [1] | | | |
| (| (ii) | | ylamine, an aromatic g a similar reaction to th | amine, cannot be prepared hat in part (i). | from [2] | | | |
| | | | | | | | | |
| | | | | | | | | |

1.

[3]

 $1094 \\ 010003$

(iii) Write a balanced equation for the reaction of butylamine with ethanoyl chloride, [1]
(iv) Phenylamine is normally prepared from nitrobenzene.
I. Give the reagents used in this preparation and a technique to separate the

3

product from the reaction mixture.

- II. When phenylamine reacts with cold nitric(III) acid (nitrous acid) a colourless solution of benzenediazonium chloride is formed. Write the formula for benzenediazonium chloride. [1]

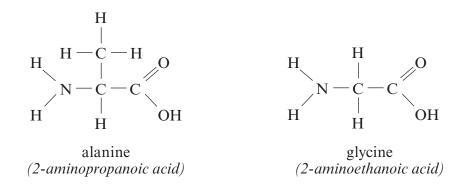
III. State the type of organic substance formed when aqueous benzenediazonium chloride reacts with an alkaline aqueous solution of naphthalene-2-ol. [1]

Total [13]

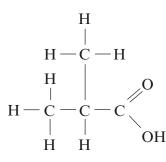
Examiner only

- Proteins and polypeptides are natural polyamides built up from α -amino acids.
 - (a) Two naturally-occurring α -amino acids are alanine and glycine.

2.



(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]

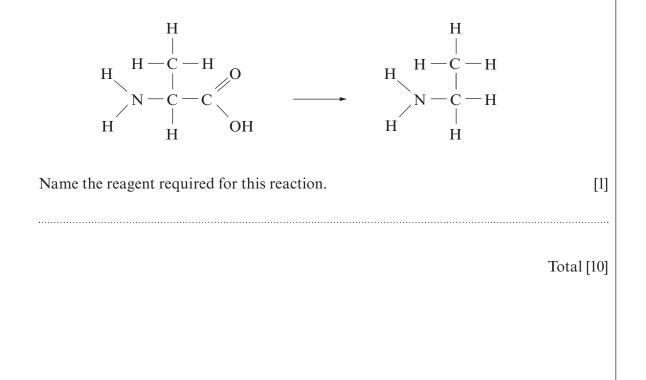
(ii) Draw the **two** possible dipeptides that can form when one molecule of glycine combines with one molecule of alanine. [2]

(iii) Circle the peptide linkage in one of your dipeptides.

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

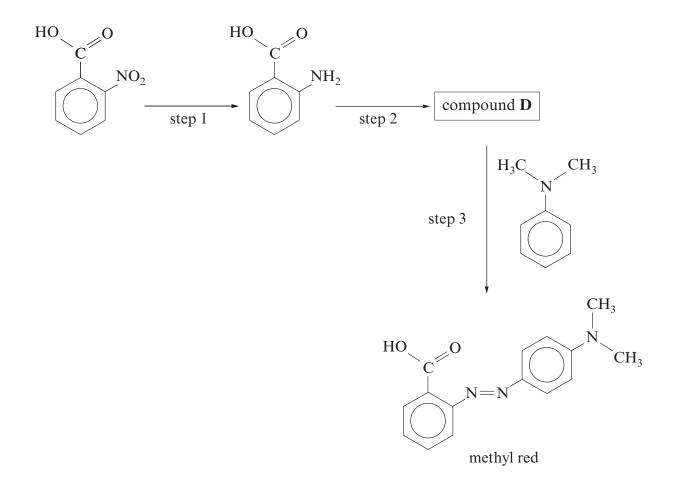
7

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



|Examiner

(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), NaNO₂, 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]

| | | | | Examiner only |
|----|-----|-------|--|------------------|
| | | | SECTION A | |
| | | | Answer all questions in the spaces provided. | |
| 1. | (a) | In p | n the information given, draw the displayed formula of each compound. arts (i)-(iii) the compounds consist of molecules that have three carbon atom art (iv) the compound has four carbon atoms. | s. |
| | | (i) | A compound that is oxidised to a ketone [| [] |
| | | | | - |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | (ii) | A neutral sweet-smelling compound [| [] |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | (iii) | An α-amino acid [| [] |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | (iv) | A hydrocarbon that exhibits E–Z isomerism [| [] |
| | | | | |
| | | | | |
| | | | | |
| | | | | |
| | | | | |

2

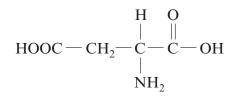
| (c) | (i) | Arrange the following molecules in order of increasing acidity. | | | | | |
|-----------------|-------|--|---------------|----------------------|---------------------|----------------|--|
| | | ethanoic acid et | hanol | ethylamine | phenol | | |
| least acidic | | | | | | most acidic | |
| | (ii) | Explain the difference | e in acid-bas | se properties of eth | ylamine and phenol. | [4] | |
| | ••••• | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | | | | | | | |
| | ••••• | | | | | | |
| | | | | | Te | otal [14] | |

4

(1094-01)

10

(b) Aspartame (*line 10*) is a methyl ester of a dipeptide formed from two α -amino acids. The structure of one of the acids is as shown below.

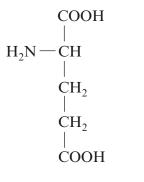


Draw the structure of the other α -amino acid.

(c) Glutamic acid (*line 16*) is amphoteric. Explain the meaning of the term *amphoteric* and why glutamic acid exhibits amphoteric behaviour. [2]



(d) Draw the skeletal formula of glutamic acid.



glutamic acid

[1]

[1]

SECTION B

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

4. (a) Today there are thousands of different polymers and they are used in a wide range of applications.

Describe the formation of **one** synthetic polymer and **one** natural polymer, both made by condensation polymerisation.

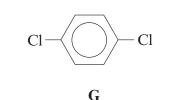
Your answer should include

- the names or structures of the starting materials required for both polymers,
- a structure which shows the repeating unit for the synthetic polymer,
- a structure which shows the relevant linkage in the natural polymer.

QWC[1]

[1]

(b) **F** and **G** are two organohalogen compounds.



F

(chloromethyl) benzene

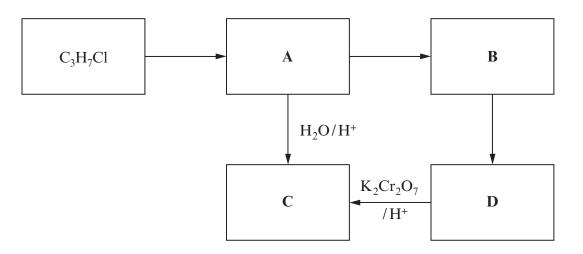
Compound \mathbf{F} is used in the manufacture of plasticizers and perfumes and behaves as a chloroalkane. Compound \mathbf{G} is used as a pesticide and as a deodorant.

- (i) Draw the displayed formula of compound **F**. [1]
- (ii) Name compound **G**.
- (iii) State the reagent(s) and condition(s) needed to substitute a chlorine atom into a benzene ring. [2]
- (iv) Describe how you could use a chemical test to distinguish between compounds F and G. Give the expected result for each compound and an explanation for any difference in their behaviour.
 [6] OWC [1]
- Benzenediazonium chloride can be prepared as follows.
 Phenylamine is dissolved in excess hydrochloric acid and the solution cooled to 5 °C.
 Aqueous sodium nitrate(III), NaNO₂, is added gradually until in excess, keeping the temperature at approximately 5 °C.
 - (i) State why the temperature is kept under 10 °C. [1]
 - (ii) Give the displayed formula of the compound that forms when benzenediazonium chloride reacts with naphthalene-2-ol in alkaline conditions. [1]
 - (iii) State what is meant by the term *chromophore*.

Total [20]

[1]

5. (a) Study the reaction scheme shown below and the other information about compounds A-D that follows.



Compound A contains a straight carbon chain and contains only carbon, hydrogen and nitrogen.

Compound **B** is basic and reacts with hydrochloric acid in a 1:1 molar ratio.

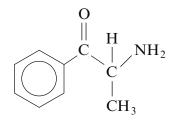
0.395 g of compound **B** in aqueous solution requires 54.00 cm³ of hydrochloric acid solution of concentration 0.100 mol dm⁻³ for complete neutralisation.

Compound **C** reacts with sodium carbonate giving off carbon dioxide.

- (i) Calculate the relative molecular mass of compound **B**. Show your working. [2]
- (ii) Identify the structures of compounds A-D, giving your full reasoning. [8]
- (b) C_3H_7Cl exists as two isomers. Sketch the low resolution NMR spectra of both isomers giving the approximate chemical shift (ppm) and the relative area of each peak. [4]

QUESTION 5 CONTINUES ON PAGES 14 AND 15

(a) Cathinone, $C_9H_{11}NO$, is a naturally-occurring psycho-active drug. 5.



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- Explain why this molecule can act as a base. (i)
- (ii) You are provided with some information about an isomer of cathinone, compound L.
 - It contains a peptide linkage.
 - It can be hydrolysed by aqueous sodium hydroxide giving primary aromatic amine M as one of the products.
 - Primary aromatic amine M reacts with nitric(III) acid (nitrous acid) to give • a phenol with the molecular formula C_7H_8O .

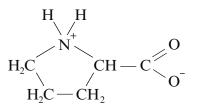
Use all this information to suggest a structural formula for compound L, giving your reasons throughout. [6] *QWC* [1]

[1]

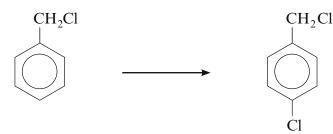
QUESTION 5 CONTINUES ON PAGES 18 AND 19

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(b) Proline is a cyclic α-amino acid. In an aqueous solution of pH 6.3, proline exists largely as its zwitterion form.



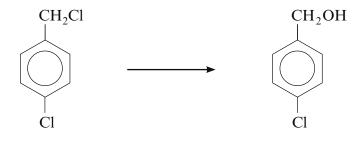
- (i) Write the structural formula of proline in its non-zwitterion form. [1]
- (ii) Proline forms two different dipeptides when it reacts with aminoethanoic acid. Give the structural formula of one of these dipeptides. [1]
- (c) (i) (Chloromethyl)benzene, $C_6H_5CH_2Cl$, reacts with chlorine in the presence of a catalyst to produce a mixture of isomers, **one** of which is 1-(chloromethyl)-4-chlorobenzene.



The mechanism of this electrophilic substitution reaction is similar to the reaction of benzene with chlorine. Give the mechanism for the reaction to produce the 4-isomer.

Your mechanism should show any necessary polarisation, curly arrows, the structure of the intermediate and how the catalyst is regenerated so that it can be used again. [4]

(ii) A student made (4-chlorophenyl)methanol by refluxing 1-(chloromethyl)-4chlorobenzene (shown in (i)) with aqueous sodium hydroxide. He obtained a 72% yield.



He wrote an outline of his method as follows.

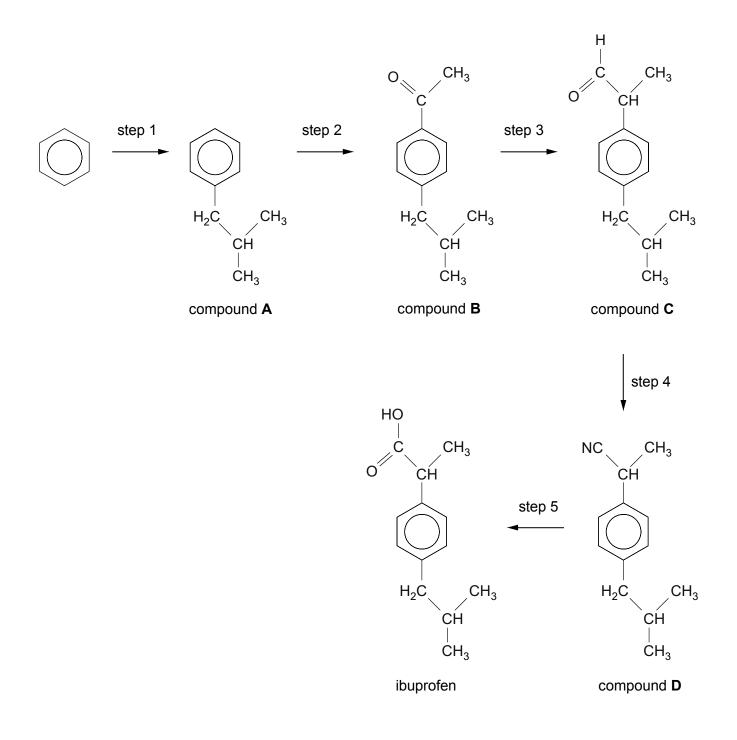
- Place 0.1 mol of the chloro-compound in a flask and add some sodium hydroxide solution of concentration 2 mol dm⁻³.
- Reflux this mixture using an electrical heater.

Suggest **two** other details that you would need to know before you could test the reliability and validity of his method. [2]

SECTION B

Answer both questions in the separate answer book provided.

4. Ibuprofen is a common drug taken as an analgesic and anti-inflammatory treatment.A possible route to the synthesis of ibuprofen is shown below.



- (b) Compounds **B** and **C** can be analysed using chemical tests.
 - Give a chemical test that would give a positive result for **both** compound **B** and compound **C**. Include reagent(s) and the observation(s) expected for a positive result.
 - (ii) Give a chemical test that would give a positive result for compound **C** but **not** for compound **B**. Include reagent(s) and the observation(s) for both compounds. [2]
- *(c)* Compound **C** shows optical isomerism. Discuss this statement. Your answer should include:
 - What is meant by optical isomerism.
 - What feature of compound **C** allows it to exhibit optical isomerism.
 - Diagrams to show the two optical isomers of compound **C**.
 - How the two optical isomers of compound **C** can be distinguished.

QWC [1]

- (d) Give the reagent(s) and condition(s) required for step 5 and classify the reaction that occurs.
 [3]
- (e) A student investigating alternative methods of producing ibuprofen suggests that it would be better to convert compound **C** into ibuprofen in a one-step process. Discuss whether this is correct.

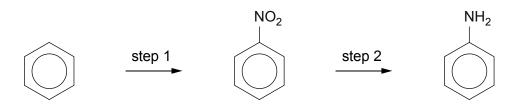
Your answer should include:

- The reagent(s) and condition(s) for a reaction expected to convert compound **C** directly into ibuprofen.
- Why it is generally better to use one step rather than two or more steps when producing a desired compound.
- A suggestion of why a two-step process is chosen for the synthesis of ibuprofen from compound **C** rather than a one-step process. [4]

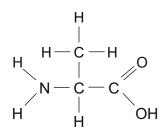
QWC [1]

Total [20]

- **5.** This question focuses on molecules that contain the $-NH_2$ group.
 - (a) Phenylamine and propylamine are both bases, with phenylamine being a weaker base than propylamine.
 - (i) Explain why both propylamine and phenylamine can act as bases. [2]
 - (ii) Give a reason why phenylamine is a weaker base than propylamine. [2]
 - (iii) Phenylamine can be prepared from benzene in a two-step process.



- I. Step 1 uses a mixture of concentrated nitric and sulfuric acids to produce NO_2^+ during the reaction. Draw the mechanism of the reaction between NO_2^+ and benzene. [3]
- II. During step 1, some dinitrobenzene is produced. Suggest a method of separating the different compounds in the product mixture. [1]
- III. Give the reagent(s) required to produce phenylamine from nitrobenzene in step 2. [2]
- (b) 1,6-diaminohexane is used to make Nylon-6,6, which is a polyamide.
 - (i) Draw the **skeletal** formula for the molecule that would be combined with 1,6-diaminohexane to make Nylon-6,6. [1]
 - (ii) Nylon is an example of a condensation polymer. Give **two** differences between condensation polymerisation and addition polymerisation. [2]



alanine (2-aminopropanoic acid)

- (i) Alanine dissolves in strong acid. Draw the carbon-containing species that would be present in this solution. [1]
- (ii) When two molecules of alanine react together they make a dipeptide. Draw the structure of this dipeptide, circling the peptide link. [2]
- (iii) Alanine has a melting temperature of 258 °C. This is much higher than compounds with molecules of a similar size such as butanoic acid, which has a melting temperature of -8 °C. Explain why the melting temperatures of these two compounds are so different. [2]
- (iv) Alanine can undergo decarboxylation. Give the reagent(s) required for this reaction and identify the organic product formed. [2]

Total [20]

Total Section B [40]

END OF PAPER

SECTION B

Answer both questions in the separate answer book provided.

4. *(a)* The formulae of the isomers phenylmethylamine and 4-methylphenylamine are shown below.



phenylmethylamine

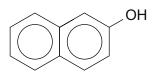
4-methylphenylamine

[1]

These compounds are colourless liquids with different boiling temperatures.

- (i) Give the name of a technique that can be used to separate these two liquids. [1]
- (ii) State and explain how the mass spectra of these two compounds would differ. [1]
- (iii) Phenylmethylamine reacts with ethanoyl chloride to give a white solid, compound **G**.
 - I Give the equation for this reaction.
 - II Compound G was purified by recrystallisation from ethanol. It has a melting temperature of 60 °C. Describe how you would recrystallise compound G from ethanol to obtain a pure dry product. You should assume that you are starting with cold ethanol and impure solid compound G. Washing of the purified solid product is unnecessary.
 [5]
 QWC [1]

(iv) 4-Methylphenylamine can be used to make an azo dye by reaction of its diazonium compound with an alkaline solution of naphthalene-2-ol.



naphthalene-2-ol

- I State how the diazonium compound can be made from 4-methylphenylamine, giving the reagents used and any essential conditions. [2]
- II Give the structural formula of the azo dye produced. [1]