



GCE A LEVEL

1410U40-1

CHEMISTRY – A2 UNIT 4

Organic Chemistry and Analysis

TUESDAY, 12 JUNE 2018 – AFTERNOON

1 hour 45 minutes plus your additional time allowance

Surname _____

Other Names _____

Centre Number _____

Candidate Number 2 _____

For Examiner's use only		
Question	Maximum Mark	Mark Awarded
Section A 1. to 5.	10	
Section B 6.	14	
7.	14	
8.	14	
9.	14	
10.	14	
Total	80	

ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:

- calculator;
- DATA BOOKLET supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink, black ball-point pen or your usual method.

Write your name, centre number and candidate number in the spaces on the front cover.

SECTION A Answer ALL questions in the spaces provided.

SECTION B Answer ALL questions in the spaces provided.

Candidates are advised to allocate their time appropriately between **SECTION A (10 MARKS)** and **SECTION B (70 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.

The assessment of the quality of extended response (QER) will take place in Q.9(a).

If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.



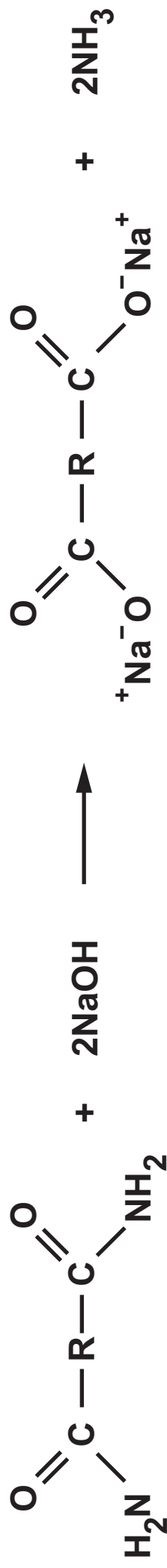
SECTION A

Answer ALL questions in the spaces provided.

1(a) Complete the equation opposite, which shows the reaction of benzaldehyde with hydrogen cyanide.

[1]

(b) Give the FORMULA of the nucleophile that takes part in the reaction shown in part (a). [1]



amide T

2. Decarboxylation occurs when a carboxylic acid is heated with sodalime.

State the name of the carboxylic acid that will produce propane when strongly heated with sodalime. [1]

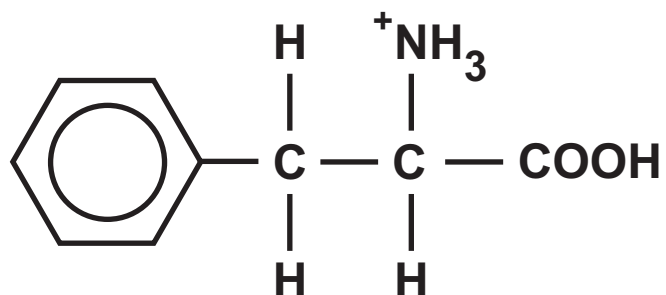
3. Ammonia is produced when an amide is heated with aqueous sodium hydroxide as shown in the equation (opposite page).

In an experiment 3.90 g of the aliphatic amide T gave 0.060 mol of ammonia.

Use this information to find the formula of the hydrocarbon group R, present in the amide T. [2]

Formula _____

4(a) In acid solution the formula of the ion formed from phenylalanine is



Give the formula of the ion formed from phenylalanine in basic solution. [1]

4(b) The melting temperatures of four compounds are shown in the table.

Compound	Melting temperature / °C
$\text{CH}_3\text{CH}_2\text{COOH}$	-21
$\text{CH}_3\text{CH}(\text{OH})\text{COOH}$	18
$\text{CH}_3\text{CHBrCOOH}$	26
$\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$	289

Explain why the melting temperature of 2-aminopropanoic acid is very much higher than the other acids in the table. [2]

5. On detonation, the explosive RDX produces carbon monoxide, steam and nitrogen.



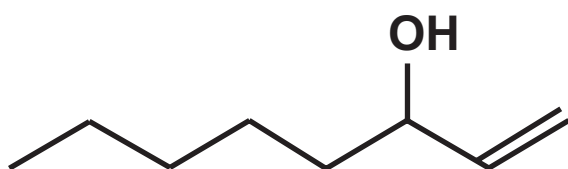
RDX

M_r 222

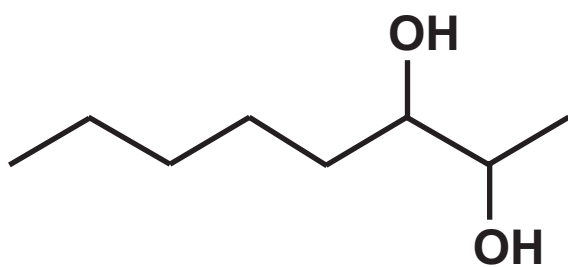
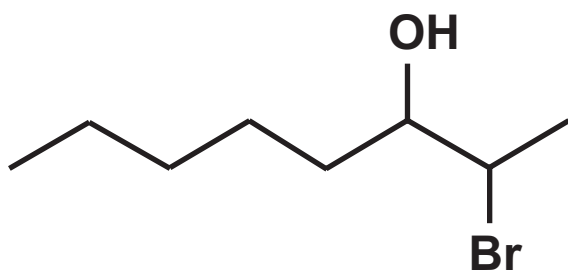
Calculate the mass of RDX that would give 1.00 m³ of gaseous products measured at 100 °C and at 1 atm. Give your answer to an APPROPRIATE number of significant figures. [2]

(1 mol of any gas occupies a volume of 30.6 dm³ under these conditions)

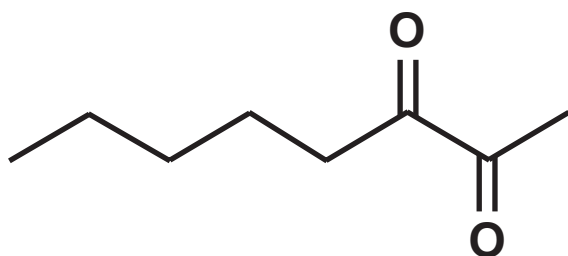
Mass of RDX = _____ g



oct-1-en-3-ol



octane-2,3-diol



octane-2,3-dione

SECTION B

Answer ALL questions in the spaces provided.

- 6(a) Oct-1-en-3-ol is a compound that attracts biting insects such as mosquitoes. It is contained in human breath and sweat and is also produced by some mushrooms.**

A sequence of reactions starting with oct-1-en-3-ol is shown opposite.

- (i) Give the molecular formula of oct-1-en-3-ol. [1]**
-

- (ii) State a reagent that can be used for Stage 2 and name the type of reaction mechanism taking place. [2]**

Reagent(s) _____

Type of reaction mechanism _____

6(a) (iii) State a reagent that can be used for Stage 3. [1]

(b) An isomer of oct-1-en-3-ol was reacted with alkaline iodine and produced a yellow precipitate.

(i) Give the formula of the yellow precipitate. [1]

(ii) Suggest a structural formula for this isomer and identify the group that enables it to produce this yellow precipitate. [2]

Structural formula

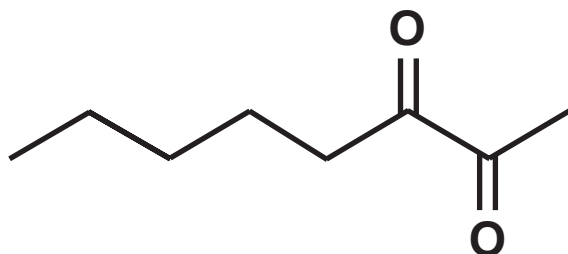
Group _____

6(c) Octane-2,3-dione is a pale yellow liquid and octane-2,3-diol is a colourless material.

(i) State a reagent that can be used to produce octane-2,3-diol from octane-2,3-dione. [1]

(ii) Suggest how the rate of the reaction in part (i) could be studied. [1]

- 6(d) The mass spectrum of octane-2,3-dione (M_r 142) shows fragmentation peaks at m/z 99, 71 and 43.

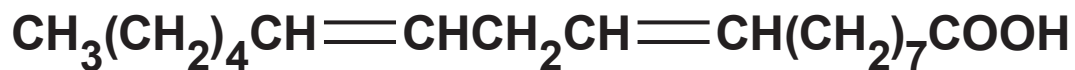


octane-2,3-dione

Identify the species responsible for these peaks.

[2]

- 6(e) Oct-1-en-3-ol is formed biochemically by the breakdown of linoleic acid.



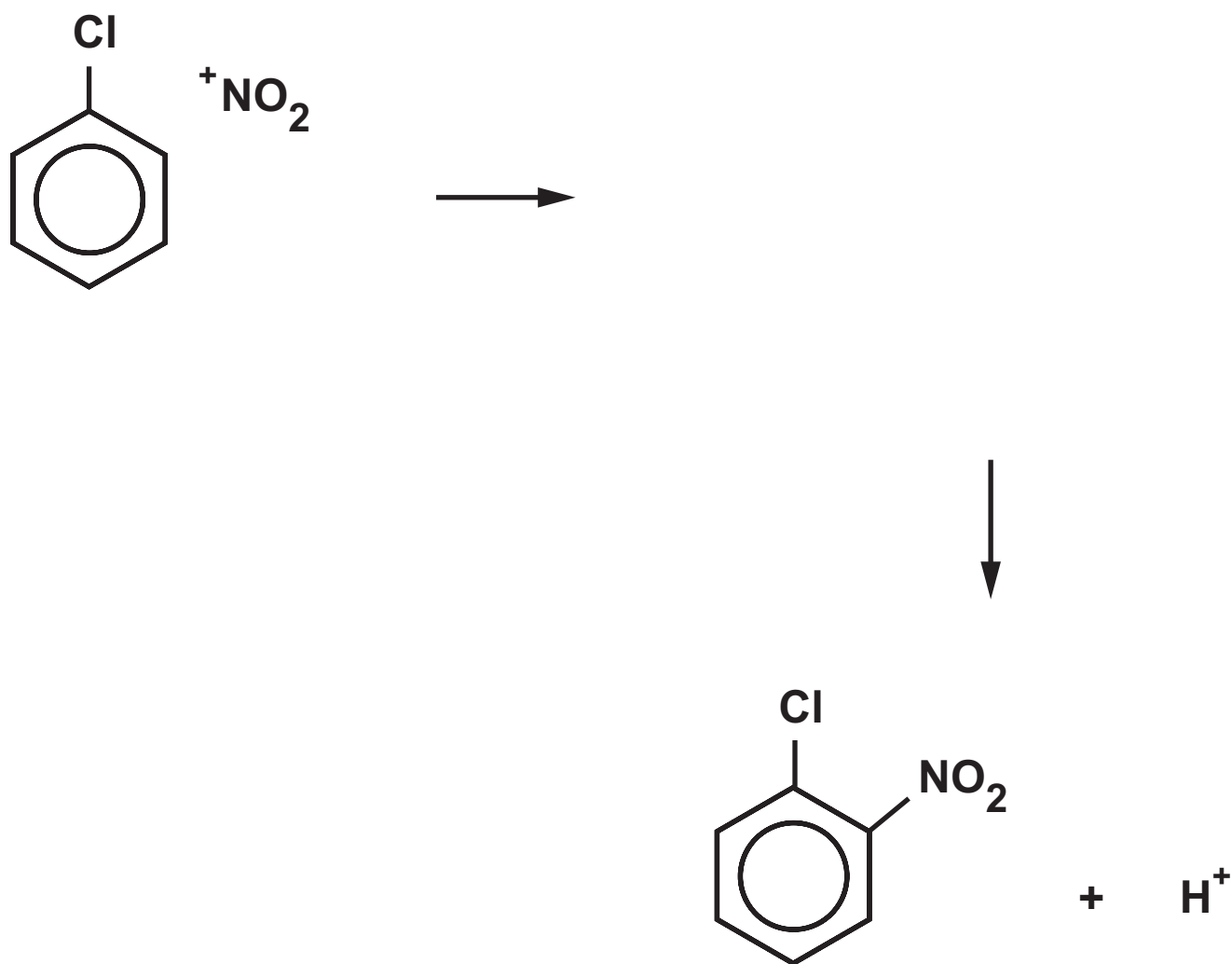
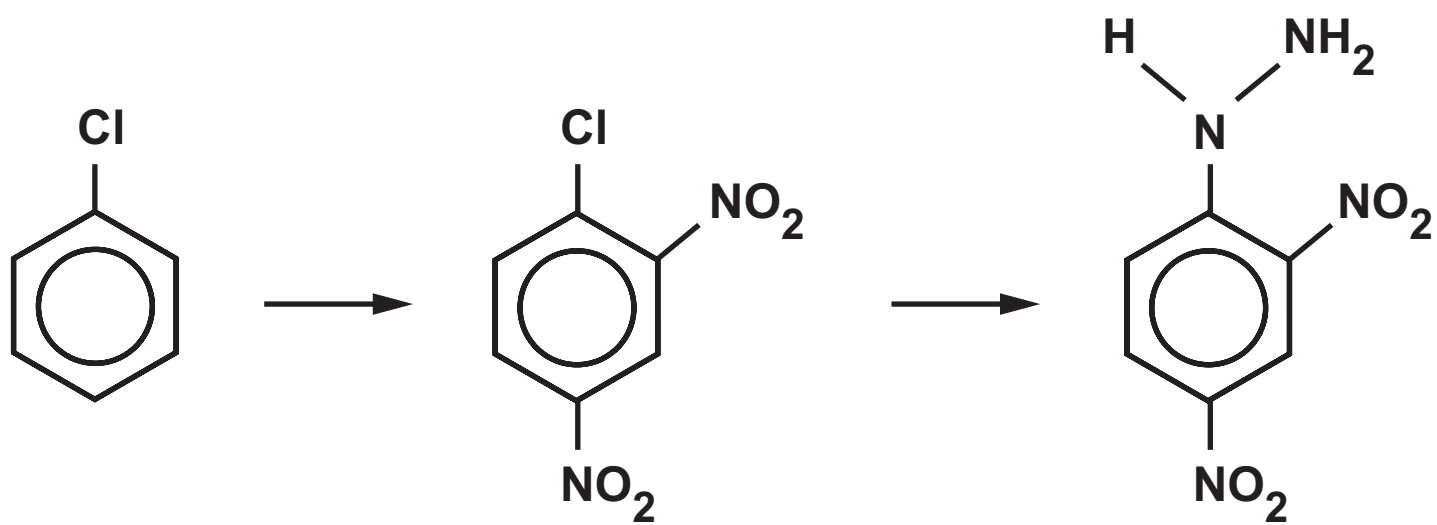
linoleic acid

The carbon to carbon double bonds in linoleic acid are reduced by hydrogen and the resulting product can then be reduced by another suitable reducing agent to give a compound of formula $\text{C}_{18}\text{H}_{38}\text{O}$.

- (i) Write the SKELETAL formula of this compound. [2]

6(e) (ii) State the name of the reducing agent used in the second stage of the reduction. [1]

14



7(a) 2,4-Dinitrophenylhydrazine (2,4-DNPH) can be made by the route shown opposite.

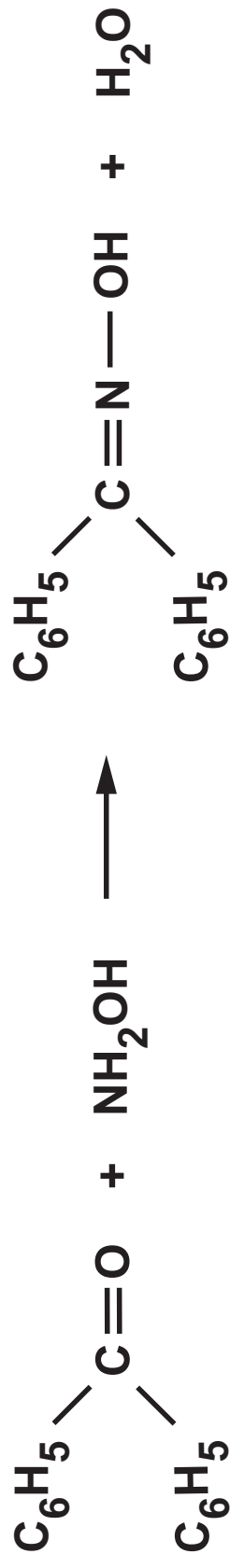
- (i) Complete the mechanism for this reaction, which shows the nitration of chlorobenzene. You should use curly arrows and also show the structure of the intermediate. [2]**
- (ii) State the type of mechanism occurring in this nitration. [1]**
-
-

(b) State the feature of 2,4-DNPH that enables it to react as a base. [1]

7(c) 2,4-DNPH can be used as a reagent to identify aldehydes and ketones.

(i) State what is seen when 2,4-DNPH is used to identify an aldehyde or a ketone. [1]

(ii) Explain why 2,4-DNPH is an appropriate reagent to use in their identification. [1]



diphenylmethanone oxime
melting temperature 143 °C

7(d) Alternative reagents can be used for this identification. One of them is hydroxylamine, NH_2OH , which produces a white crystalline solid when it reacts with an aldehyde or ketone.

For example with diphenylmethanone (opposite page)

In an experiment, impure diphenylmethanone oxime was recrystallised from flammable methanol (boiling temperature 65°C).

Outline a SAFE procedure to obtain pure dry crystals of diphenylmethanone oxime using methanol as the solvent. You should assume that all the material present in the crude oxime is soluble in methanol. [5]

14

8(a) For a number of years CFCs were used in refrigeration and in air conditioning. The use of these compounds is in decline as they damage the ozone layer. A typical CFC is chlorotrifluoromethane.

Give an equation that shows the formation of a chlorine radical from chlorotrifluoromethane. [1]

- 8(b) CFCs are being replaced by hydrofluorocarbons (HFCs) such as difluoromethane, which can be made by the reaction of dichloromethane with hydrogen fluoride in the presence of a catalyst.



One problem with this reaction is that chlorofluoromethane is also produced.

The table below shows the percentage of the organic products formed (and unreacted dichloromethane) for various starting ratios of the reactants.

Mole ratio HF : CH ₂ Cl ₂	Percentage composition of mixture / %		
	CH ₂ Cl ₂	CH ₂ ClF	CH ₂ F ₂
26 : 1	1.5	6.5	92.0
22 : 1	1.8	10.2	88.0
19 : 1	3.0	11.0	86.0
16 : 1	4.5	11.5	84.0

- 8(b) (i) Write a statement that links the mole ratio of HF : CH₂Cl₂ with the yield of difluoromethane. [1]
-
-

- (ii) In an experiment using 0.040 mol of CH₂Cl₂, the yield of CH₂F₂ was 89.0%. Calculate the mass of difluoromethane produced. [2]

Mass = _____ g

STAGE 1 – an exothermic process



STAGE 2 – an endothermic process



8(c) 1,1,1,2-Tetrafluoroethane is an HFC that is made from trichloroethene and hydrogen fluoride in a two-stage vapour phase process shown opposite.

(i) Suggest, giving a reason, whether a high or low pressure should be used in STAGE 1.

[1]

(ii) Suggest, giving a reason, whether a high or low temperature should be used in STAGE 2. [1]

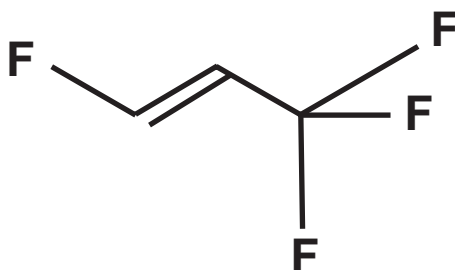
- 8(c) (iii) The boiling temperatures of the organic products formed after each stage are shown below.

Compound	Boiling temperature / °C
1,1,1-trifluoro-2-chloroethane	7
1,1,1,2-tetrafluoroethane	-26

The final product tends to be contaminated with some of the chlorocompound formed in the first stage.

State the name of the method that can be used to separate these two compounds and suggest how this could be carried out in practice. [2]

- 8(d) The use of HFCs is now declining as these compounds are contributing to global warming. Compounds such as HFOs (hydrofluoroolefins) are under development as suitable replacements. One such HFO is 1,3,3,3-tetrafluoropropene.



- (i) Explain why 1,3,3,3-tetrafluoropropene exists as *E/Z* isomers. [1]

8(d) (ii) The addition of hydrogen bromide to 1,3,3,3-tetrafluoropropene results in two structural isomers, each of molecular formula $C_3H_3BrF_4$.

I. State the type of mechanism occurring in this reaction. [1]

II. These two compounds are formed in APPROXIMATELY EQUAL AMOUNTS in this reaction.

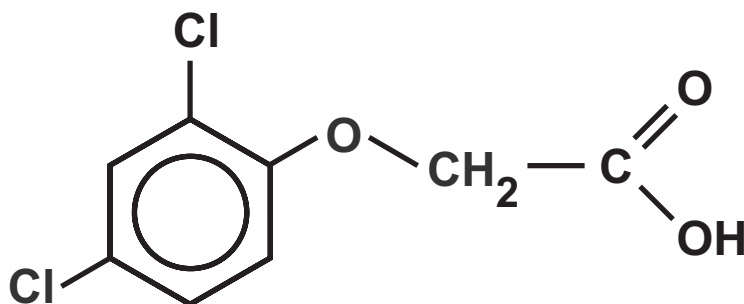
Suggest why this ratio is different to that found in the reactions of other alkenes. [1]

8(d) (iii) Both the compounds formed in part (ii) will rotate the plane of plane polarised light.

Give the formula of BOTH compounds indicating the chiral centre in both. [2]

- 8(d) (iv) Draw the two mirror image forms of the compound 1-bromo-1,2-difluoroethane, $\text{CHBrFCH}_2\text{F}$. [1]

- 9(a) A solid compound is believed to be the herbicide 2,4-dichlorophenoxyethanoic acid (2,4-D).



The following results were obtained when this compound was analysed.

- The percentage by mass of chlorine present was 32.1
- A solution of the compound reacted with sodium hydrogencarbonate to give a colourless gas
- 4.09 g of the compound was dissolved in a suitable solvent and the solution made up to 250 cm³. A 25.0 cm³ sample of this solution reacted with 24.70 cm³ of aqueous sodium hydroxide of concentration 0.0750 mol dm⁻³
- Refluxing a sample of the compound with aqueous sodium hydroxide did NOT show the presence of chloride ions in the resulting mixture

9(b) An ester can be hydrolysed by heating it with aqueous sodium hydroxide solution.

(i) Give the equation for the hydrolysis of methyl ethanoate. [1]

9(b) (ii) The hydrolysis reaction can be used in a quantitative way to find the relative molecular mass of an ester.

A known mass of an ester is refluxed with a known volume of sodium hydroxide solution of concentration 1.0 mol dm^{-3} and the excess sodium hydroxide remaining after hydrolysis is determined by an acid-base titration.

The following results were obtained.

Mass of ester used = 1.76 g

Volume of aqueous sodium hydroxide added = 50.0 cm³ (V_2)

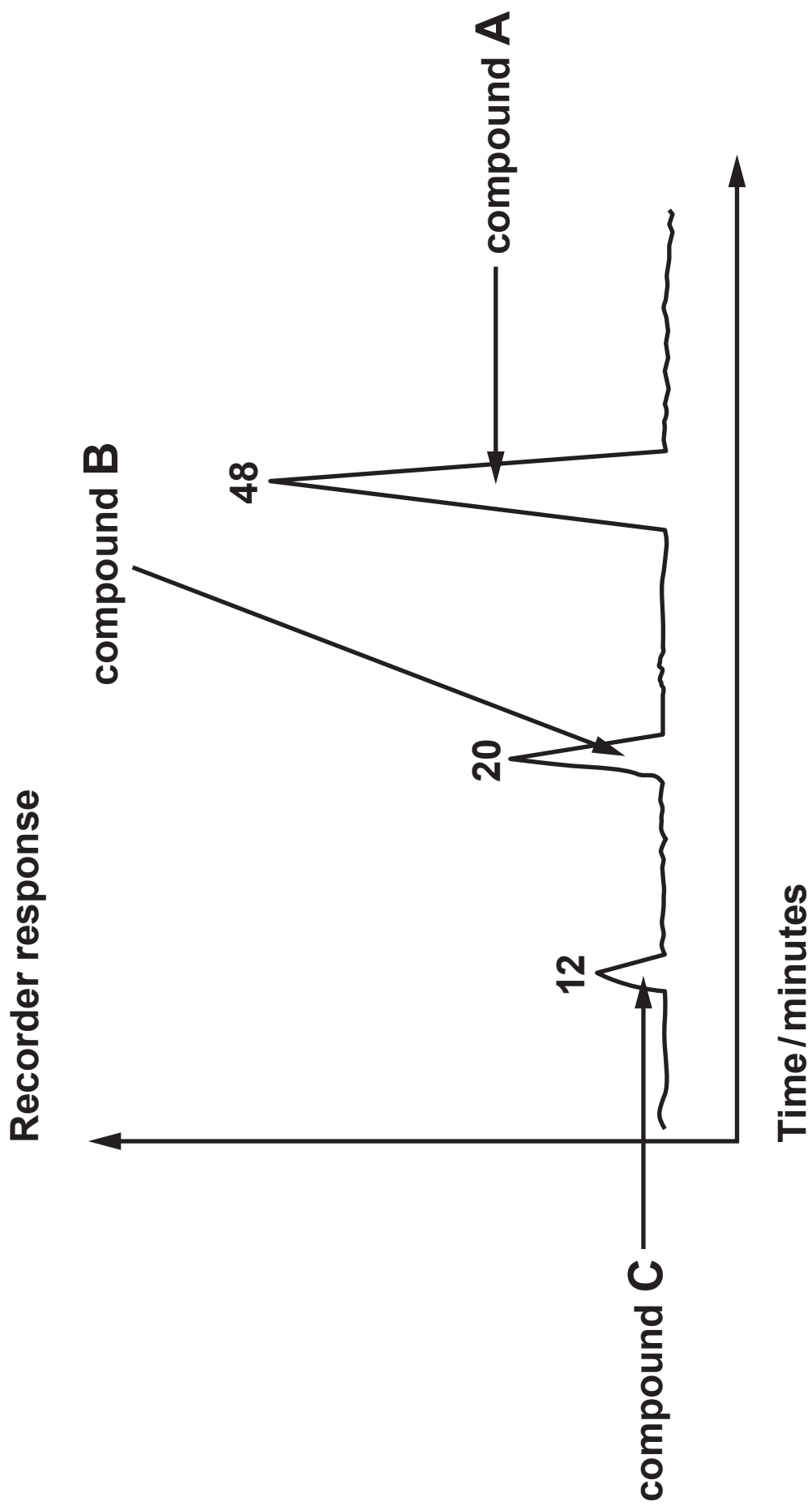
Volume of aqueous sodium hydroxide remaining after hydrolysis = 30.0 cm³ (V_1)

- I. Use the formula below to calculate the M_r of the ester. [1]

$$\text{mass of ester} = \frac{M_r \text{ of the ester} \times (V_2 - V_1)}{1000}$$

$M_r =$ _____

- 9(b) (ii) II. The ester reacts with Tollens' reagent to give a silver mirror. Use this information and the M_r of the ester found in part I to suggest a formula for the ester. Give a reason for your answer. [2]



9(b) (iii) Esters of ethanoic acid with the formula $\text{CH}_3\text{COOC}_5\text{H}_{11}$ are used to give fruity flavours to confectionery.

- I. The material used for this flavouring is often a mixture of esters having the formula above.

The diagram opposite shows a gas chromatogram of a typical mixture.

Use the peak area data to calculate the percentage of compound **A** that is present in the mixture. [1]

Percentage = _____ %

9(b) (iii)

II. The peak areas shown give the molar percentage and in this case also the percentage by mass of each component present in the mixture.

Explain why the molar percentage of each compound **CANNOT** be used to find the percentage by mass of each component if the relative molecular mass of each component differs. [1]

Compound	Name	R in $\text{CH}_3\text{—C}(=\text{O})\text{—O—R}$	Boiling temperature / °C
A	2-methylbutyl ethanoate	$\text{—CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	134
B	3-methylbutyl ethanoate	$\text{—CH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$	142
C	pentyl ethanoate	$\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	147

9(b) (iv) The boiling temperatures of compounds A, B and C in part (iii) are shown in the table opposite.

Suggest a reason for the difference in boiling temperatures between compounds A and C. [1]

- 9(b) (v) Compound **A** is made by heating 2-methylbutan-1-ol and ethanoic acid in the presence of concentrated sulfuric acid.

State the name of another organic compound that could be formed if concentrated sulfuric acid reacted with 2-methylbutan-1-ol. [1]

Stage	Reagent used	Structural formula of product
1		
2		
3		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$

10(a) Butylamine can be made from propan-1-ol in a three-stage process.

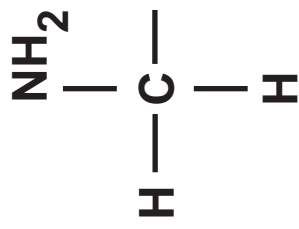
Give the reagent used and the structural formula of the product for each stage in the table opposite.

[3]

(b) Below 10 °C, phenylamine reacts with nitric(III) acid, HNO_2 , to give a benzenediazonium compound, which can react with phenol to give an azo dye.

(i) State how nitric(III) acid is prepared for use in this reaction. [1]

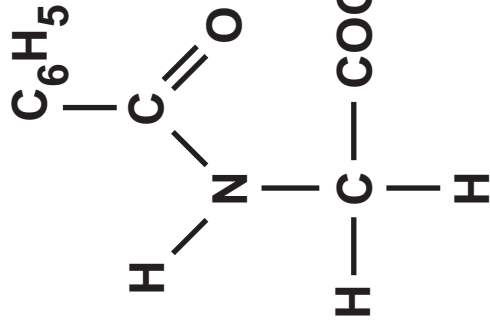
(ii) Give the equation for the reaction of benzenediazonium chloride with phenol to produce an azo dye. [1]



+



+



+



benzoyl chloride

hippuric acid

10(c) Hippuric acid, so called because it is found in the urine of horses, can be made by reacting aminoethanoic acid and benzoyl chloride as shown opposite.

In an experiment the percentage yield was 90%.

Benzoyl chloride is only slowly hydrolysed by alkalis. A teacher suggested the following idea for increasing the percentage yield.

‘The experiment could be carried out in the presence of aqueous sodium hydroxide.’

Comment on the validity of this suggestion and any effect it may have on the yield.

Explain your answer. [1]



10(d) A straight chain α -amino acid of general formula $R-CH(NH_2)COOH$ reacts with nitric(III) acid to give nitrogen gas as shown opposite.

In an experiment 7.87 g of the amino acid was dissolved in water and the solution made up to 500 cm^3 . A 25.0 cm^3 sample of this solution was reacted with an excess of nitric(III) acid and gave 73.5 cm^3 of nitrogen measured at 298 K and 1 atm pressure.

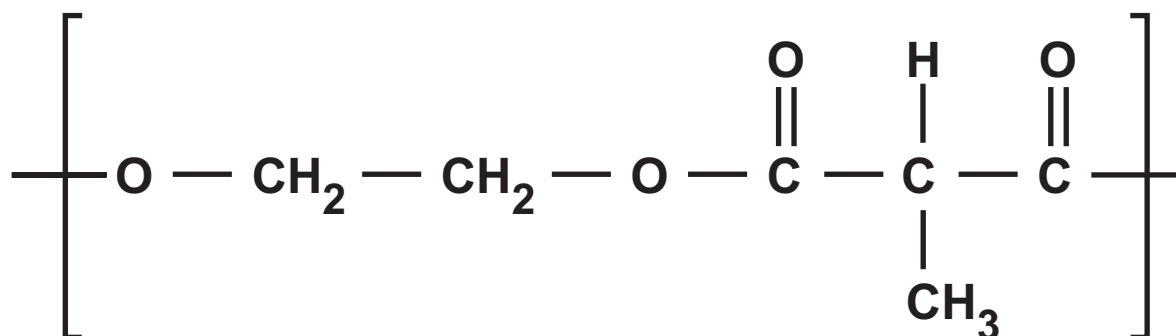
Calculate the molar mass of the amino acid and hence its structural formula. [4]

Molar mass = _____

45

Structural formula

10(e) Polyesters can be made from a dicarboxylic acid and a diol, such as ethane-1,2-diol.



polyester E

- (i) State the name of the dicarboxylic acid that reacts with ethane-1,2-diol to give polyester E. [1]

- (ii) Complete the table opposite to describe the high resolution ^1H NMR spectrum of polyester E. [3]

14

Protons	Splitting pattern	Relative peak area
—CH ₂ —CH ₂ —		
—CH—		
—CH ₃		

