

A LEVEL

Examiners' report

CHEMISTRY A

H432

For first teaching in 2015

H432/02 Summer 2019 series

Version 1

Contents

Introduction	4
Paper 2 series overview	5
Section A overview	6
Question 3	6
Question 4	6
Question 5	7
Question 10	8
Question 12	9
Question 13	10
Question 14	10
Question 15	11
Section B overview	12
Question 16 (a) (i)	12
Question 16 (a) (ii)	12
Question 16 (b) (i)	13
Question 16 (b) (ii)	14
Question 16 (b) (iv)	14
Question 16 (b) (v)	15
Question 17 (a) (i)	17
Question 17 (a) (ii)	19
Question 17 (b) (i)	20
Question 18 (a) (i)	21
Question 18 (a) (ii)	22
Question 18 (b)	23
Question 18 (c)	23
Question 18 (d)	24
Question 18 (e) (i)	24
Question 18 (e) (ii)	26
Question 19 (a) (i)	27
Question 19 (a) (ii)	29
Question 19 (b) (i)	30
Question 19 (b) (iii)	32
Question 19 (b) (iv)	34
Question 20 (a) (i)	36
Question 20 (a) (ii)	37

Question 20 (a) (iii)	37
Question 20 (b) (i)	38
Question 21	39



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Introduction

Our examiners' reports are produced to offer constructive feedback on candidates' performance in the examinations. They provide useful guidance for future candidates. The reports will include a general commentary on candidates' performance, identify technical aspects examined in the questions and highlight good performance and where performance could be improved. The reports will also explain aspects which caused difficulty and why the difficulties arose, whether through a lack of knowledge, poor examination technique, or any other identifiable and explainable reason.

Where overall performance on a question/question part was considered good, with no particular areas to highlight, these questions have not been included in the report. A full copy of the question paper can be downloaded from OCR.

Paper 2 series overview

H432/02 is the second of the three examination components for GCE Chemistry A. This component is focused on organic chemistry and brings together topics from modules 4 and 6 of the specification, including relevant practical techniques. There is a synoptic element to all of the three of the A Level examinations and as such this paper also contains some content of modules 1 and 2 set in the context of organic chemistry.

The paper consists of two sections comprised of multiple choice and a mixture of short and long response questions respectively.

Candidate performance overview

Candidates who did well on this paper generally:

- Demonstrated knowledge of concepts and techniques used in organic chemistry: 16(b)(v), 18(a)(i), 18(b), 18(e)(i)(ii), 19(a)(i) and 20(a)(i)(iii).
- Applied knowledge of reactions to unfamiliar compounds, including those with more than one functional group: 17(a)(i), 18(a)(ii) and 19(b)(iv).
- Drew clear diagrams to show reaction mechanisms: 16(a)(i), 19(b)(iii) and 20(b)(i).
- Solved problems with logical and clear working: 17(a)(ii), 18(c), 18(d) and 21.

Candidates who did less well on this paper generally:

- Produced written responses that lacked accuracy and precision: 16(a)(ii), 16b(v) and 19(a)(i).
- Found it difficult to apply what they had learnt to unfamiliar compounds: 17(a)(ii), 18(e)(i), and 19(b)(iv).
- Showed unclear presentation of organic structures and mechanisms: 16(a)(i), 19(b)(i), and 19(b)(iii).
- Showed unclear setting out of working in calculations: 17(a)(ii), 18(e)(i), 18(d) and 21.

There was no evidence that any time constraints had led to a candidate underperforming and scripts where there was no response to the final question also had large sections of the paper which had not been tackled.

Note

From this series students have been provided with a fixed number of answer lines and an additional answer space. The additional answer space will be clearly labelled as additional, and is only to be used when required. Teachers are encouraged to keep reminding students about the importance of conciseness in their responses. Please follow this link to our SIU

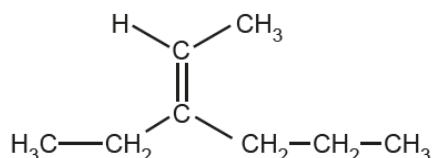
<https://www.ocr.org.uk/administration/support-and-tools/siu/alevel-science-538595/>

Section A overview

Section A comprises 15 multiple choice questions that assess many different areas of the specification, including practical techniques. This section of the paper is worth 15 marks.

Question 3

- 3 What is the name of the compound below?



- A 3-Propylpent-2-ene
 B 3-Propylpent-3-ene
 C 3-Ethylhex-2-ene
 D 4-Ethylhex-4-ene

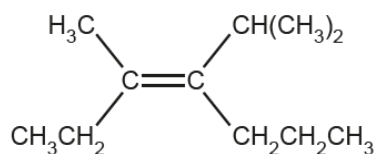
Your answer

[1]

The majority of candidates were able to select 3-ethylhex-2-ene (C) as the correct name of the compound. A common incorrect response was D.

Question 4

- 4 The structure of a stereoisomer is shown below.



Which term correctly describes this stereoisomer?

- A *cis*-
 B *trans*-
 C *E*-
 D *Z*-

Your answer

[1]

This question proved difficult. Many candidates identified that this structure is an *E* stereoisomer (C) but a significant number of responses selected D. Candidates are encouraged to draw out the groups to determine the first point of difference when applying the Cahn Ingold Prelog (CIP) priority rules.

**OCR support**

OCR has a worksheet which can help support students' understanding of Cahn Ingold Prelog priority rules, available here:
<http://www.ocr.org.uk/Images/208569-cip-rules-activity.doc>.

Question 5

- 5 Which types of bonds are broken and formed in the reaction of ethene and bromine?

	Types of bond broken	Types of bond formed
A	σ	π
B	π	σ
C	σ and π	π
D	σ and π	σ


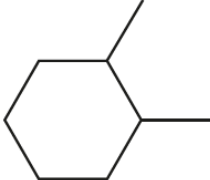
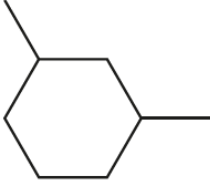

Your answer

[1]

This is a demanding question. The best responses drew the first step of the mechanism near the table. This showed both the π bond in ethene and the σ bond in bromine breaking in addition to a σ bond forming between carbon and bromine atoms. Although many candidates correctly selected D, option B was a good distractor and was the most commonly seen incorrect response.

Question 10

10 Which compound shows 4 peaks in its carbon-13 NMR spectrum?

A	
B	
C	
D	

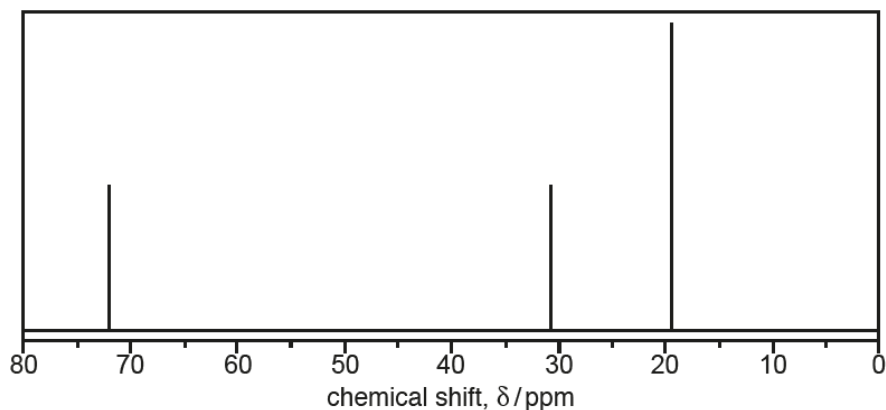
Your answer

[1]

Most candidates correctly selected B as the compound that would show four peaks in the ^{13}C NMR spectrum. Many candidates annotated the structures, indicating the different carbon environments with a circle. This proved a good strategy. Common incorrect responses included C and D which were seen in roughly equal proportions.

Question 12

12 A compound produces the ^{13}C NMR spectrum below.



Which compound could have produced this spectrum?

- A Propane
- B 2-Methylbutane
- C 2-Methylpropan-1-ol
- D 2-Methylpropan-2-ol

Your answer

[1]

Many candidates identified that 2-methylpropan-1-ol (C) produced the ^{13}C NMR spectrum shown. The majority of successful responses included diagrams showing the structures of the compounds to choose from. The most frequently seen incorrect response was D.

Question 13

13 A carbonyl compound is reacted with NaBH_4 .

Which compound(s) could be formed?

- 1 2-Methylpentan-2-ol
- 2 2-Methylpentan-1-ol
- 3 3-Methylpentan-2-ol

- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

Your answer

[1]

This question discriminated well, with the higher ability candidates correctly selecting C. The most common incorrect response was A.

Question 14

14 Which chemical(s) can react with phenol?

- 1 Potassium hydroxide
- 2 Ethanoyl chloride
- 3 Nitric acid

- A** 1, 2 and 3
B Only 1 and 2
C Only 2 and 3
D Only 1

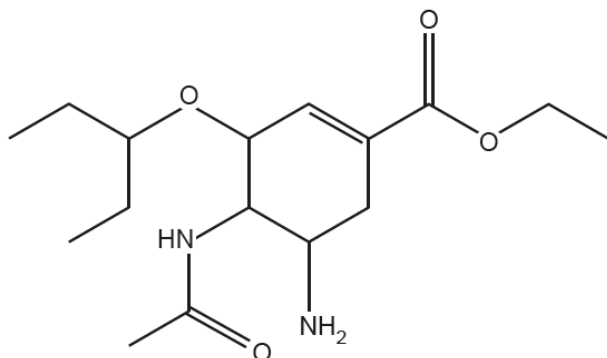
Your answer

[1]

This question proved difficult. Many candidates correctly deduced that all three chemicals would react with phenol and selected A. Some candidates did not recognise that phenol would react with HNO_3 without the need for a catalyst and selected B. Other candidates did not consider the weak acidity of phenol and selected C.

Question 15

15 The structure of a compound used to treat influenza is shown below.



Which functional group(s) is/are in a molecule of the compound?

- 1 Ester
- 2 Secondary amide
- 3 Ketone

- A 1, 2 and 3
- B Only 1 and 2
- C Only 2 and 3
- D Only 1

Your answer

[1]

Most candidates were able to identify the functional groups correctly and selected B. Some candidates opted for A, presumably assuming the C=O at the top of the structure was a ketone. A small, but significant number of candidates chose option C.

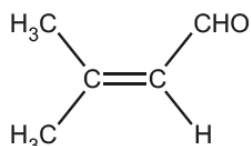
Section B overview

Section B includes a mixture of short answer and extended response questions, including two questions marked using a level of response mark scheme (18(e)(i) and 21). This section of the paper is worth 85 marks.

Question 16 (a) (i)

16 This question is about unsaturated aldehydes and alcohols.

(a) 3-Methylbut-2-enal, shown below, is used as a food flavouring.



3-methylbut-2-enal

3-Methylbut-2-enal is reacted with hydrogen bromide, forming a mixture of two organic products.

One of the organic products forms in a much greater quantity than the other organic product.

(i) Outline the reaction mechanism for the formation of **one** of the organic products.

Include curly arrows and relevant dipoles.

[4]

Candidates were very familiar with this electrophilic addition mechanism, so the majority of candidates scored three or four marks. Common errors included inaccurate curly arrows from either the carbon-carbon double bond or the bromide ion or the omission of key detail such as the partial charges on HBr or the charge on the bromide ion.

Question 16 (a) (ii)

(ii) Explain why one of the organic products forms in a much greater quantity than the other organic product.

.....

 [2]

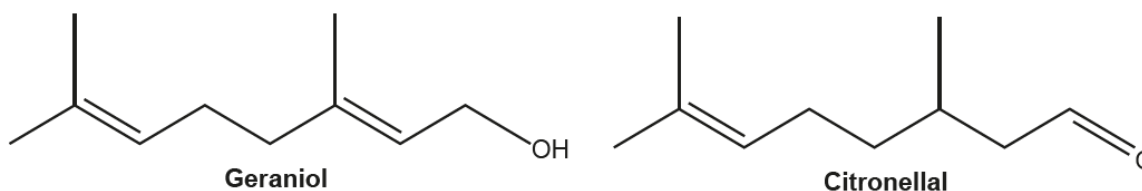
This question required candidates to apply their knowledge of Markownikoff's rule to explain the formation of a major product in the reaction in part (a)(i). The majority of candidates recognised that the stability of the intermediate was responsible for one of the products being formed in a greater quantity, and most scored at least one mark. The best responses recognised that, in the context of the reaction in (a)(i), a tertiary carbocation would form the major product. Other response talked more generally about the major product (without identifying that the tertiary carbocation in the mechanism is responsible). Lower ability candidates focused their response on the stability of the product and did not discuss the intermediate at all.

**OCR support**

A topic exploration pack on electrophilic addition and Markownikoff's rule, including activities to assess student understanding, is available here: <http://www.ocr.org.uk/Images/336551-electrophilic-addition-and-markownikoff-s-rule.doc>

Question 16 (b) (i)

- (b) Geraniol and citronellal, shown below, are isomers present in 'citronella oil', used as an insect repellent.



- Geraniol and citronellal are structural isomers of each other.
 - They also show stereoisomerism.
- (i) Describe how the observations from a chemical test would distinguish between geraniol and citronellal.

.....

.....

.....

..... [2]

Almost all candidates were able to describe a suitable test to distinguish between geraniol and citronellal and most scored both marks. The most common choice was to use Tollens' reagent to identify the aldehyde group in citronellal by the formation of a silver mirror. Other candidates opted for 2,4-dinitrophenylhydrazine to differentiate the carbonyl compound from the alcohol.

Question 16 (b) (ii)

- (ii) What is the molecular formula of geraniol?

..... [1]

Many candidates were able to determine the correct molecular formula of geraniol as $C_{10}H_{18}O$. A small but significant proportion of the candidates gave a structural formula, showing each C atom in turn, rather than grouping atoms of the same element together. Candidates are encouraged to practice giving different types of formulae for a range of organic compounds to make sure that each type is understood, and to check to ensure they are providing the type of formula that the question is asking for.

Question 16 (b) (iv)

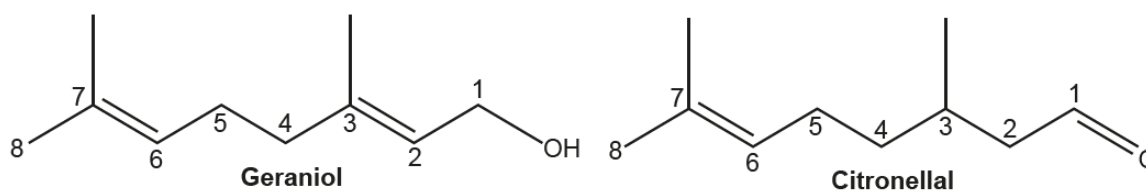
- (iv) Explain the term **stereoisomerism**.

.....
.....
..... [1]

Most candidates were able to explain the term stereoisomerism succinctly. However, a significant number of candidates referred to stereoisomers as having the same molecular formula, rather than being more precise and stating that they are compounds with the same structural formula.

Question 16 (b) (v)

(v) The structures of geraniol and citronellal are repeated below with the carbon atoms numbered.



Explain the types of stereoisomerism shown by geraniol and citronellal.

In your answer,

- refer to the numbered carbon atoms in the structures above
- draw diagrams clearly showing any stereoisomers.

.....

.....

.....

.....

.....

.....

Geraniol stereoisomers

Citronellal stereoisomers

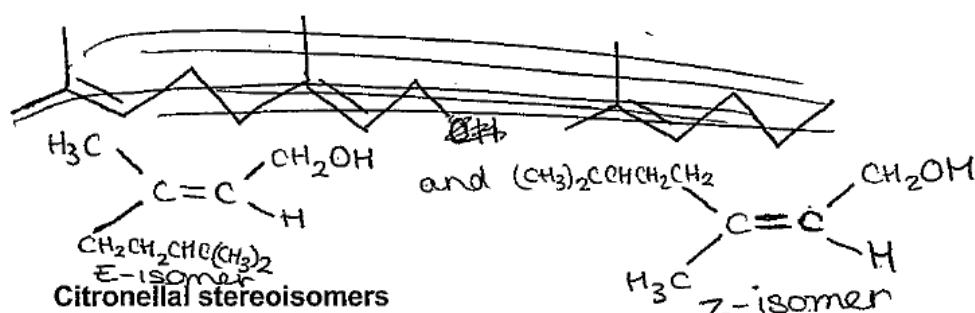
[4]

This question, which discriminated well, required candidates to apply their knowledge of stereoisomerism to geraniol and citronellal. The majority of responses focused on *E/Z* isomerism, as shown in Exemplar 2. Many candidates were able to show the structure of the *Z* isomer of geraniol and scored at least one mark. Stronger responses were able to explain this type of isomerism as the result of the carbon-carbon double bond between carbon atoms 2 and 3. Common errors included attributing *E/Z* isomerism to the double bond between carbon atoms 6 and 7 or use of *cis/trans* to describe the isomers (the latter of which was ignored by the mark scheme as it does not apply to geraniol). The best responses also identified the chiral carbon atom in citronellal and were able to show the optical isomers appropriately.

Exemplar 1

Geraniol shows *E/Z* isomerism across ~~the~~ the double carbon-carbon bond between 2 and 3, this is because 2 and 3 are both joined to 2 different groups and the double bond has restricted rotation. Citronellal has no stereoisomers because it only contains a carbon-carbon double bond between 6 and 7 but carbon 7 is not attached to 2 different groups.

Geraniol stereoisomers



This response identifies that geraniol has *E/Z* isomers and provides a correct explanation with reference to the carbon-carbon double bond between carbon atoms 2 and 3. So marking points one and two were given. The candidate recognises that the double bond between carbon atoms 6 and 7 would not cause isomerism in both compounds. Unfortunately this response overlooks the chiral carbon in citronellal and incorrectly states that it has are no stereoisomers. This question highlights the challenge of a linear specification, where content from different modules may be assessed within the same question. Candidates are likely to encounter these two types of stereoisomerism in different years of their course. They should therefore be encouraged to make links between the different modules to help develop their understanding.

Question 17 (a) (i)

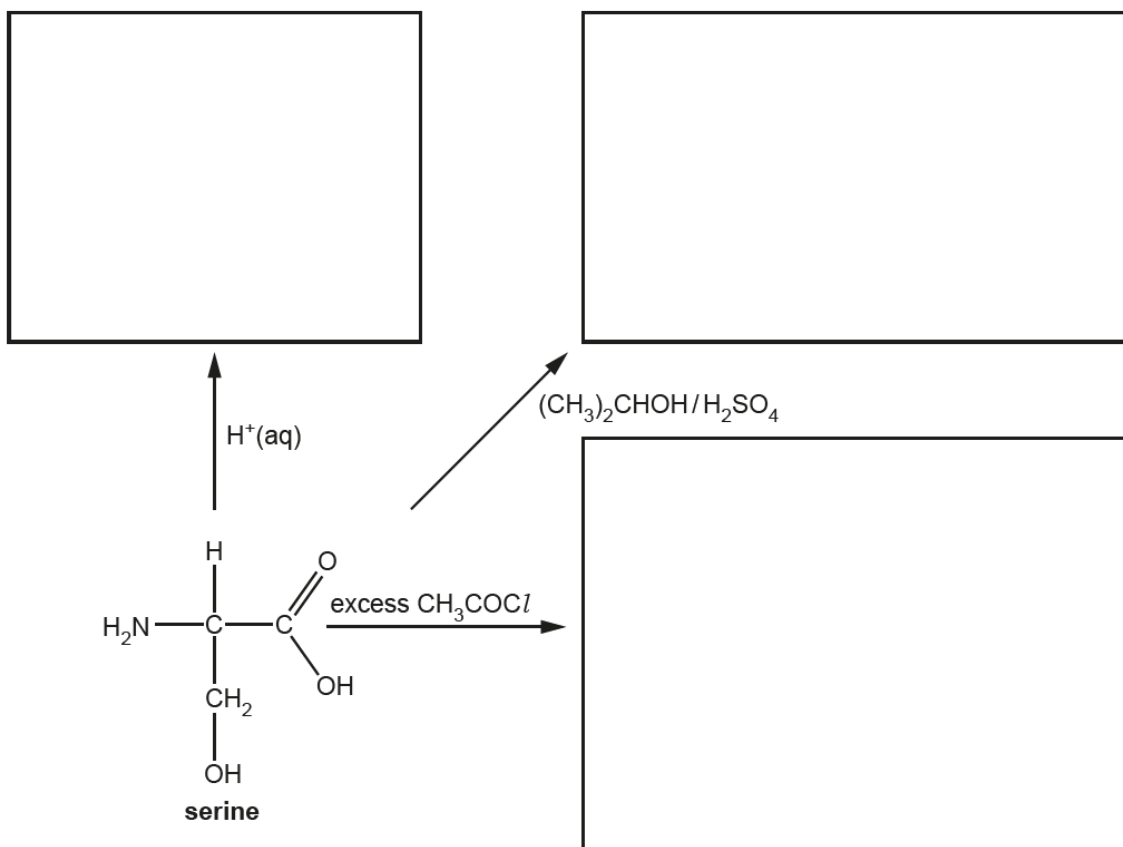
17 This question is about α -amino acids, $\text{RCH}(\text{NH}_2)\text{COOH}$.

(a) Table 17.1 shows the R groups in four amino acids.

Amino acid	R group
alanine (ala)	CH_3-
serine (ser)	HOCH_2-
leucine (leu)	$(\text{CH}_3)_2\text{CHCH}_2-$
glycine (gly)	$\text{H}-$

Table 17.1

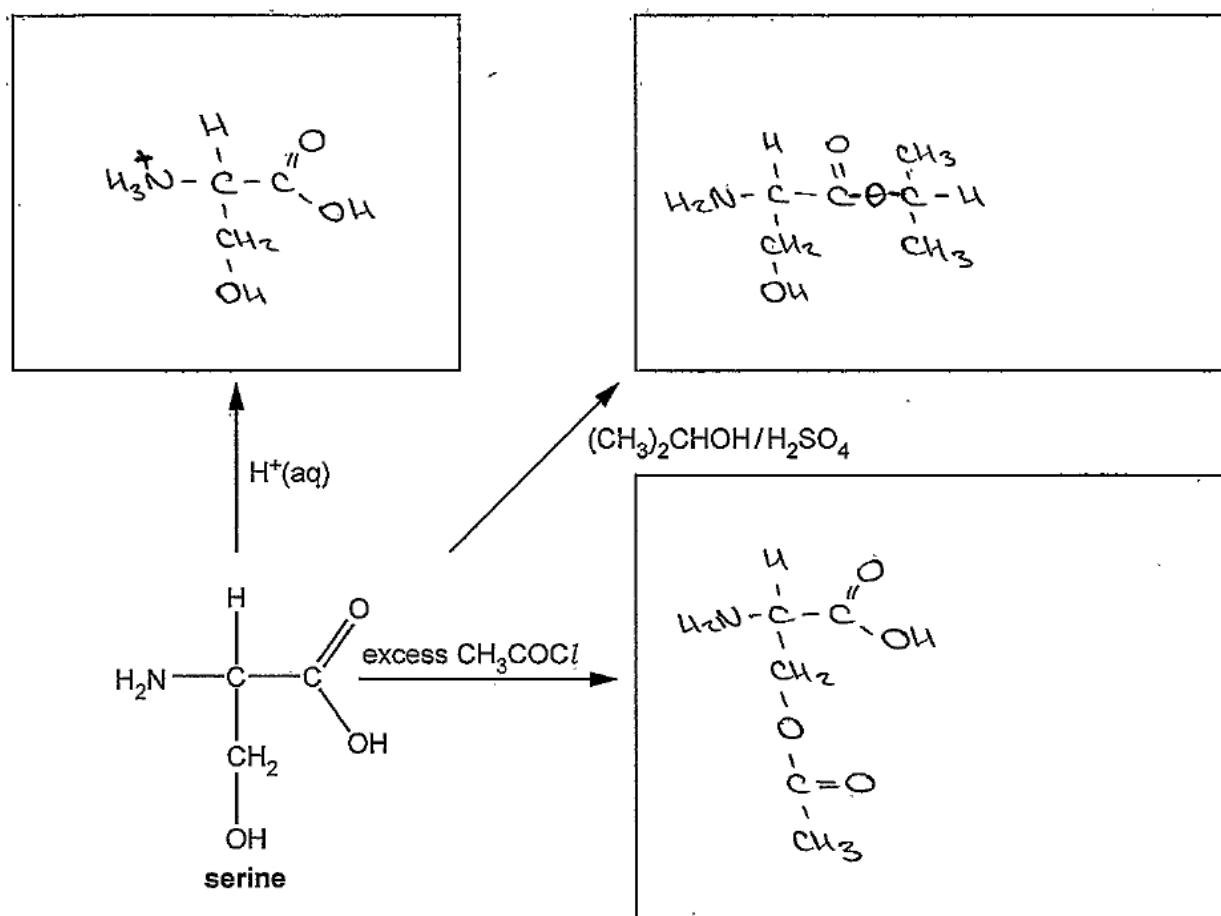
(i) In the boxes, draw the organic products for the reactions of serine shown below.



[4]

This question focused on the reactions of the different functional groups in serine. Candidates are familiar with these reactions and most candidates scored at least two marks. These were achieved by the formation of the ammonium ion by reaction with H^+ and the formation of the ester from $(\text{CH}_3)_2\text{CHOH}$. Determining the organic product from the reaction of serine with excess CH_3COCl proved more difficult. Some candidates realised that the OH of serine's R group would react and others drew the amide formed from the reaction of the NH_2 group. The best responses showed both conversions and scored full marks. Lower ability responses often showed organic products containing the Cl atom from the ethanoyl chloride rather than the CH_3CO group.

Exemplar 2



This response scored three marks. The candidate has drawn correct organic products for the reaction of serine with H^+ and $(\text{CH}_3)_2\text{CHOH}$. The product from the reaction of excess CH_3COCl shows the formation of an ester but not the formation of the amide. This product was seen often by examiners and scored one mark. If an amide group had been shown this response would have received full marks. Notice the candidate has presented their organic products clearly with the structures drawn in a similar manner to serine shown in the question. This is a good strategy to avoid errors and omissions when drawing organic structures.

Question 17 (a) (ii)

(ii) A student is provided with one of the four amino acids in **Table 17.1**.

A student carries out a titration with a standard solution of hydrochloric acid to identify the amino acid. The student's method is outlined below.

- The student dissolves 5.766 g of the amino acid in water and makes the solution up to 250.0 cm³ in a volumetric flask.
- The student titrates this solution with 25.0 cm³ of 0.150 mol dm⁻³ hydrochloric acid.
- 21.30 cm³ of the amino acid solution were required for complete neutralisation of the hydrochloric acid.

Determine which amino acid the student used.

[4]

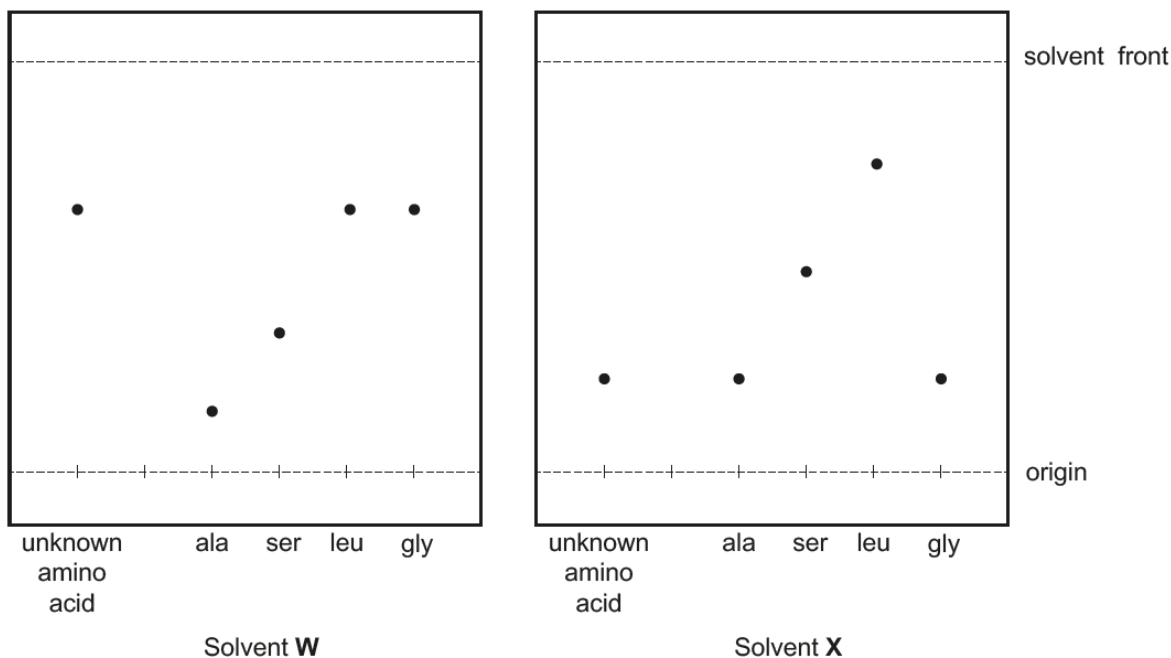
Candidates are confident in tackling titration analysis and the majority of responses were well structured. Most candidates used the results to determine the *Mr* of the unknown amino acid and hence identify it as leucine. However, other approaches were also seen and these were given full credit if correct. A common error was incorrect scaling to determine the amount of amino acid used to make the 250 cm³ solution. A significant number of responses simply multiplied the number of moles of acid by ten rather than using a factor of 250/21.30. Error carried forward marks were available and so the majority of candidates scored 3 or 4 marks.

Question 17 (b) (i)

(b) The student is provided with another amino acid.

The student attempts to identify the unknown amino acid using chromatography.

The student obtains two TLC chromatograms of the unknown amino acid and the four amino acids in Table 17.1, using two different solvents, **W** and **X**.



(i) What is the R_f value of serine (ser) in solvent **W**?

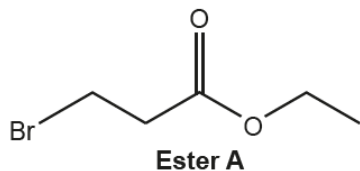
$R_f = \dots\dots\dots$ [1]

Candidates are familiar with the calculation of R_f values and this question was answered very well. Although almost all candidates showed appropriate working as part of their response some candidates gave the final answer to only one significant figure and did not receive credit. Candidates were expected to give their answer to a number of significant figures appropriate to the measurements they had made, so a minimum of two significant figures was expected. The mark scheme allowed a response within a range, rather than a specific value, and most candidates scored in this part.

Question 18 (a) (i)

18 This question is about esters.

(a) The structure of ester **A** is shown below.



(i) What is the systematic name of ester **A**?

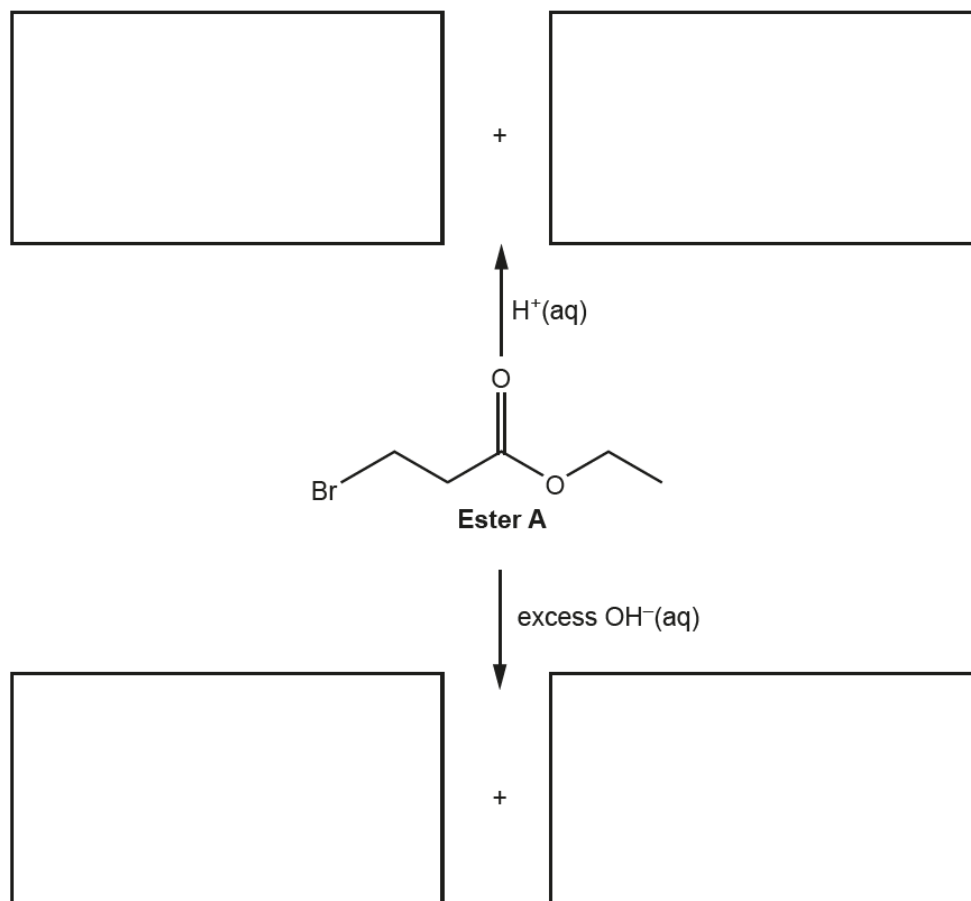
..... [1]

This demanding question discriminated well. The most able candidates were able to apply the nomenclature rules to name ester **A** correctly as ethyl 3-bromopropanoate. Common incorrect responses included ethyl 1-bromopropanoate and ethyl 4-bromopropanoate.

Question 18 (a) (ii)

- (ii) In the boxes, draw the organic products for the reactions of the functional groups in ester **A** shown below.

Each reaction forms two organic products.

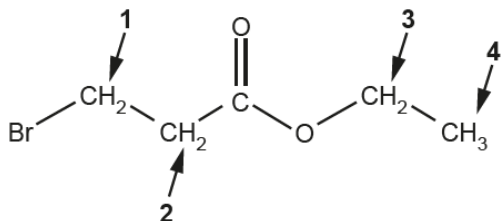


[5]

This question required candidates to apply their knowledge of hydrolysis reactions to ester **A**. The majority of candidates were able to show 3-bromopropanoic acid and ethanol in the top two boxes to secure two marks. The organic products from the alkaline hydrolysis proved more difficult. Many candidates identified ethanol as a product in one of the lower boxes but lower ability responses showed the ethoxide ion. Some candidates drew the 3-bromopropanoate ion as the other product. Higher ability candidates realised that the Br atom would be replaced by an OH group and the best responses showed the correct carboxylate ion. Examiners were encouraged by the number of excellent responses seen and the majority of candidates scored 4 or 5 marks.

Question 18 (b)

(b) The protons in ester **A** are in four different environments, labelled 1–4 on the structure below.



Complete the table to predict the **proton** NMR spectrum of ester **A**.

Proton environment	Chemical shift	Splitting pattern
1		
2		
3		
4		

[4]

This question was answered well and most candidates scored full marks. A common error was the chemical shift of environment **2**, which was sometimes shown as 9.0-10.0. Some candidates gave incorrect splitting patterns for environment **2**, stating it would give a singlet, rather than a triplet. This is presumably the result of focusing on the carbon atom to the right of the environment with no H atoms. Candidates should be reminded to consider adjacent carbon atoms on both sides of a particular environment, rather than just looking in one direction.

Question 18 (c)

(c) Compound **B** is a structural isomer of ester **A**.

- Compound **B** reacts with aqueous sodium carbonate.
- The ^{13}C NMR spectrum of **B** has 4 peaks.

Draw a possible structure for compound **B**.

[1]

This question required candidates to use both pieces of information to deduce that **B** was a carboxylic acid with two equivalent carbon atoms. Many candidates were able to suggest a suitable structure. However some candidates did not use all the information and it was common to see responses that showed an ester or a straight chain carboxylic acid.

Question 18 (d)

- (d) A polyester is formed from 200 molecules of 4-hydroxybenzoic acid.

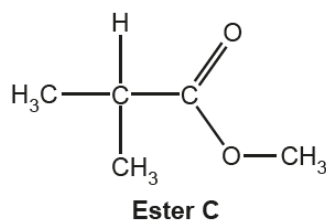
What is the relative molecular mass, M_r , of the polyester?

$$M_r = \dots\dots\dots \text{ g mol}^{-1} \text{ [2]}$$

A variety of responses was seen in this demanding question. In general candidates adopted one of two approaches. The most common was to multiply the M_r of 2-hydroxybenzoic acid by 200 and then subtract the mass of the 199 water molecules removed during polymerisation. The other approach used the M_r of the repeat unit. This was multiplied by 200 and the mass of H and OH at each end of the polymer was added to give the final answer. Many candidates were successful with the first step of their approach, but the best responses included the second step taking into account the M_r of water. A significant number of candidates used an incorrect value for the M_r in their first step. Candidates are advised to draw out the structure of a compound before determining the M_r . This is particularly important when only a name is given in the question.

Question 18 (e) (i)

- (e)* A student intends to synthesise ester **C**.



- (i) Plan a two-stage synthesis to prepare 12.75 g of ester **C** starting from 2-methylpropanal, $(\text{CH}_3)_2\text{CHCHO}$. Assume the overall percentage yield of ester **C** from 2-methylpropanal is 40%.

In your answer include the mass of 2-methylpropanal required, reagents, conditions and equations where appropriate.

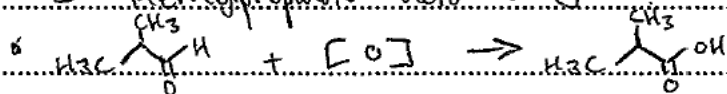
Purification details are **not** required.

[6]

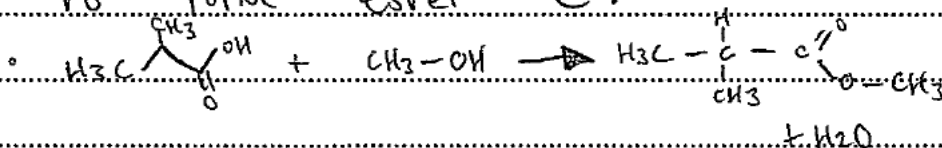
This question was marked using a level of response mark scheme. Most candidates gave a response worthy of at least Level 2 (3-4 marks) by either providing the synthetic steps with reagents and/or equations for the synthesis of ester **C** as well as calculating the mass of 2-methylpropanal required. Exemplar 3, below, shows a frequently seen Level 2 response. The best performing candidates determined the mass correctly and showed the synthesis efficiently, using equations to communicate the preparation of ester **C** and received Level 3 (5-6 marks). Some responses focused solely on the 2-methylpropanal and suggested it would be both oxidised and reduced with each of the products being used to form an ester. Others omitted the mass calculation or gave only a partial synthesis. Such responses received Level 1 (1-2 marks).

Exemplar 3

① Oxidation of 2-methylpropanal to form 2-methylpropanoic acid using $K_2Cr_2O_7/H^+$ under reflux.



② Esterification of 2-methylpropanoic acid with methanol to form ester C.



Ester C: 2-methylpropanoic acid
O.C.H: 1

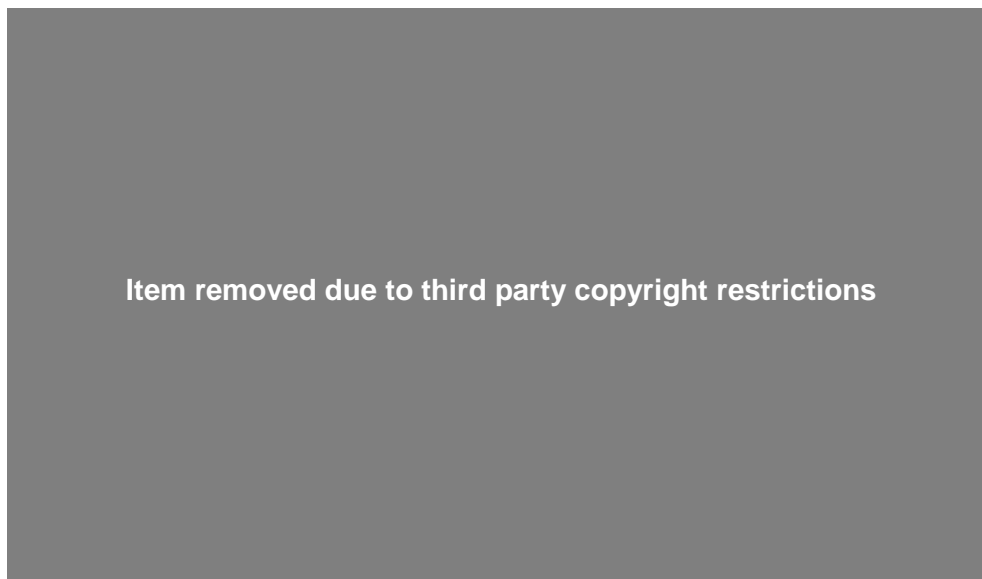
$$\therefore \text{2-methylpropanal mass required} = \frac{12.75}{0.4} = 31.875 \text{ g} = 31.88 \text{ g (to 2 d.p.)}$$

This response includes an excellent description of the synthesis of ester C. Each step is labelled clearly with the most of the reagents and conditions stated and correct equations. The candidate makes little progress with the calculation of the mass of 2-methylpropanal required, completing only the first step. This response satisfies the Level 2 criteria. The information provided is relevant and presented with a clear logical structure and was therefore given the upper mark within the level and achieved four marks.

The presentation of the synthesis by equations rather than words is an excellent strategy. Candidates are advised to adopt such an approach in questions like this as it allows them develop a clear line of reasoning without the need to write lots of unnecessary text.

Question 18 (e) (ii)

(ii) The mass spectrum of ester **C** is shown below.



Suggest possible structures for the species responsible for peaks **Y** and **Z** in the mass spectrum.

Y	Z

[2]

Most candidates were able to provide a correct structure for each of the ions responsible for the peaks labelled **Y** and **Z**. Some candidates omitted the charge, or included 'end bonds'. These responses were able to achieve one mark if both fragments were correct. So the majority of candidates scored one or two marks in this part.

Question 19 (a) (i)

19 This question is about benzene.

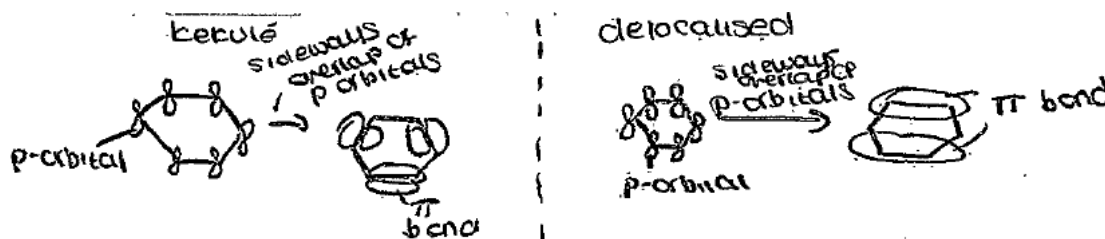
- (a) Over time, the Kekulé and delocalised models have been used to describe the bonding and structure of a benzene molecule.
- (i) Describe, in terms of orbital overlap, the similarities and differences between the bonding in the Kekulé model and the delocalised model of benzene.

.....

..... [3]

Candidates found this question difficult. The majority of the cohort referred to the overlap of p orbitals in either the Kekulé or delocalised model. The best responses developed this idea further and made reference to π bonds above and below the bonding carbon atoms. Although some candidates were able to describe the difference between the two models, the responses of others lacked detail. Describing conceptual ideas, such as orbital overlap and π bonds, is understandably tricky. Candidates are advised to draw diagrams. These serve as a good basis from which to construct a written response. Exemplar 5 shows how effective the use of diagrams can be.

Exemplar 4



Similarities - Both models involve the sideways overlap of adjacent p-orbitals. Both give a pi bond with a trigonal planar shape with bond angles of 120° . Both C_6H_6 .

Differences - Delocalised pi bonds ^{sideways} overlap forms delocalised pi electrons π ring with 6 electrons over 6 carbons, whereas Kekulé leads to 3 pi bonds of 2 electrons localised over 2 carbons ^{for} each π bond. Delocalised structure gives more stability.

This response starts with a diagram for both the Kekulé and delocalised models of benzene. Each diagram is clear and shows the p orbitals and π bonds separately. This is an excellent response for future candidates to follow.

The candidate's written response is effectively a description of the diagrams they have drawn and describes the similarities and differences between these two models clearly. This response scored full marks and demonstrates the best style of response seen in this part.

Question 19 (a) (ii)

- (ii) Experimental evidence led to the general acceptance of the delocalised model over the Kekulé model.

Describe **two** pieces of evidence to support the delocalised model of benzene.

.....
.....
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.....
.....
.....
.....
..... [2]

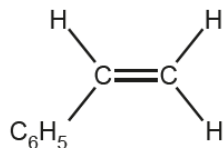
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Candidates were well prepared for this question and the majority of the cohort scored two marks. The most common piece of evidence given was the lack of reactivity of benzene with bromine, with candidates citing the need for a catalyst for the reaction to occur. Responses also included reference to carbon-carbon bond lengths as well as the enthalpy of hydrogenation. A small but significant proportion of the cohort referred to hydration rather than hydrogenation.

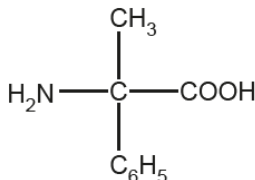
Question 19 (b) (i)

- (b) Benzene can be used as the starting material for the synthesis of compounds **D** and **E**, shown below.

In the diagrams C_6H_5 is a phenyl group.



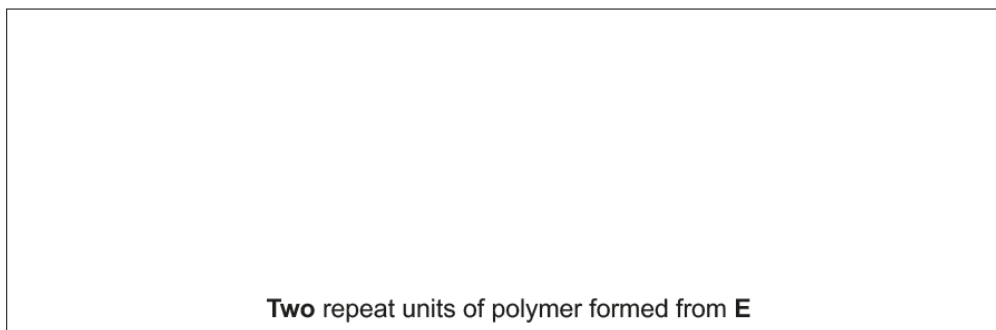
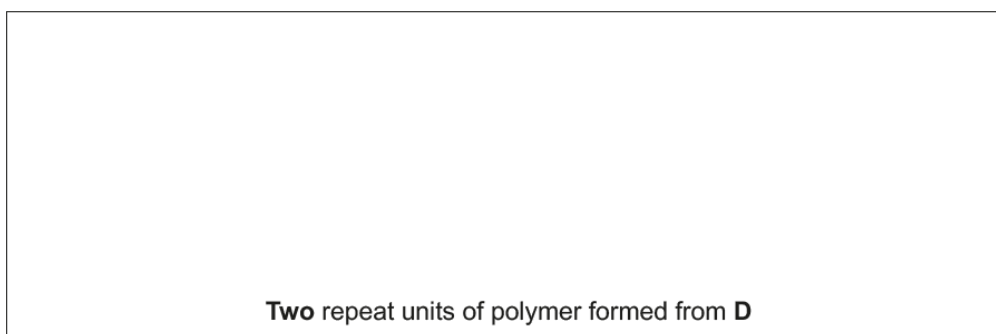
compound D



compound E

Compounds **D** and **E** can be converted into polymers.

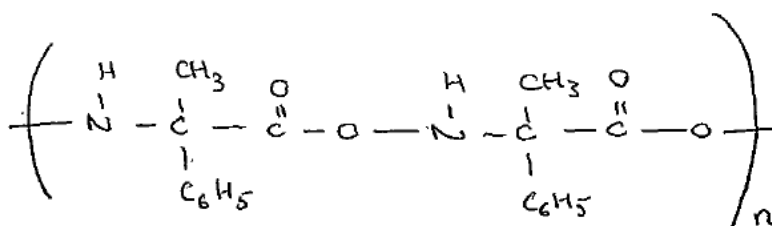
- (i) Draw **two** repeat units of these polymers.



[3]

The majority of candidates were able to draw two repeats units of the polymer formed from **D** and scored at least one mark. While most candidates drew the polymer from **E** correctly, securing full marks, some candidates were unable to show the amide link correctly. This common error is demonstrated in Exemplar 6.

Exemplar 5

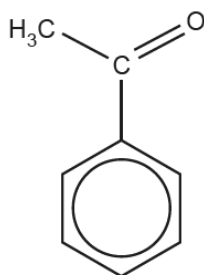


Two repeat units of polymer formed from E

This response demonstrates a common error seen by examiners. The candidate has included an O atom as part of the amide link. So they have also included an O atom before the 'end bond'. This is a costly error as the candidate is unable to be given either of the marks available for this polymer.

Question 19 (b) (iii)

- (iii) In the synthesis of compounds **D** and **E**, benzene is first reacted with ethanoyl chloride, CH_3COCl , to form phenylethanone, shown below.



phenylethanone

The reaction takes place in the presence of aluminium chloride, AlCl_3 , which acts as a catalyst.

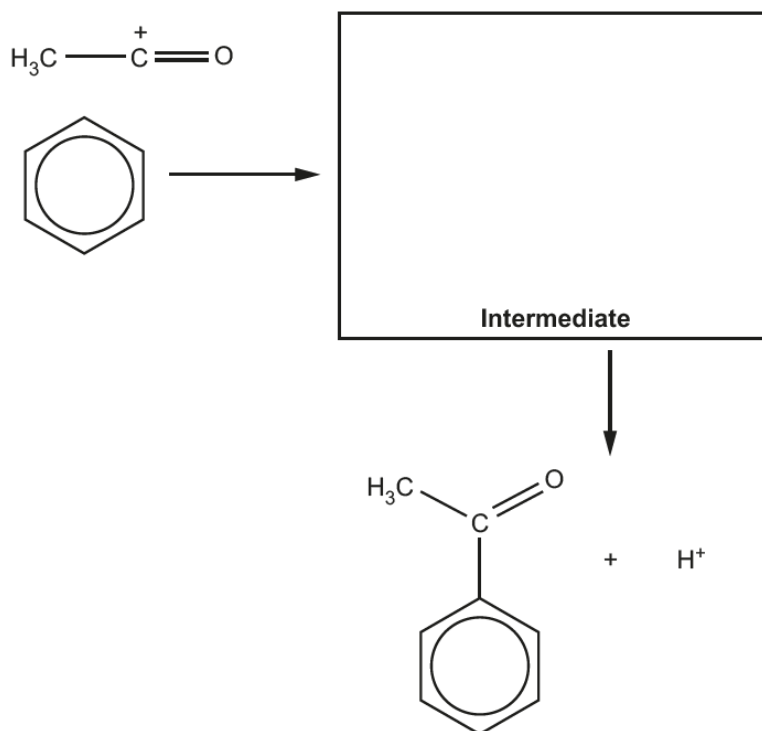
In the mechanism for this reaction,

- ethanoyl chloride first reacts with aluminium chloride to form the $\text{CH}_3\text{-C}^+=\text{O}$ cation
- the $\text{CH}_3\text{-C}^+=\text{O}$ cation then behaves as an electrophile.

Complete the mechanism for the reaction.

Include equations to show the role of the AlCl_3 catalyst, relevant curly arrows and the structure of the intermediate.

Formation of electrophile

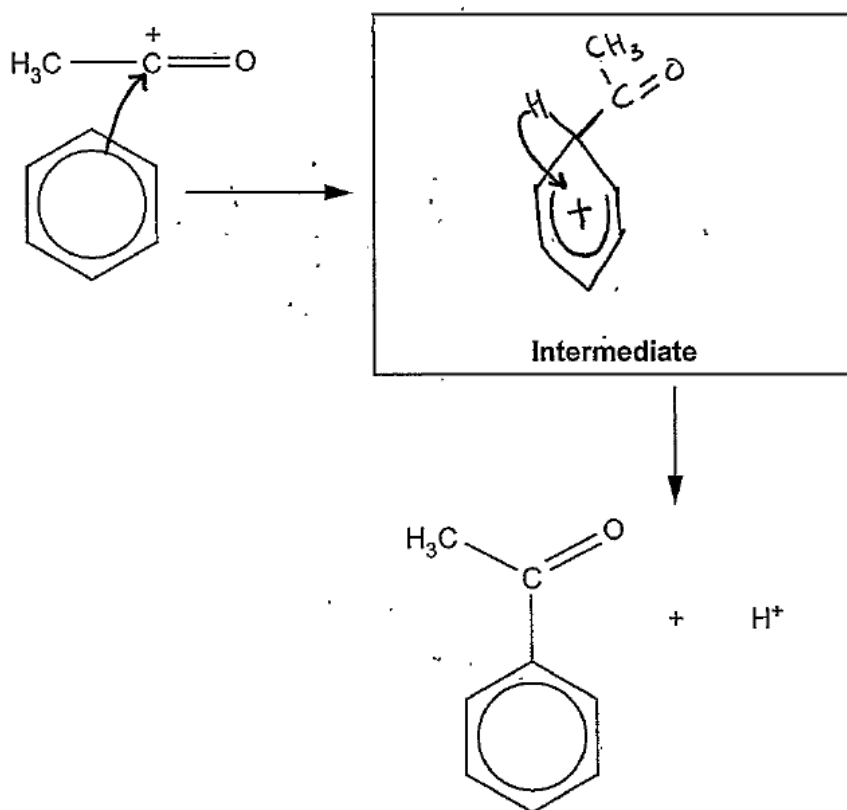


Regeneration of catalyst

This question required candidates to apply their knowledge of the mechanism of electrophilic substitution to the formation of phenylethanone from benzene. Examiners were encouraged by the number of excellent responses to this question, with the majority of candidates securing four out of five marks. Common errors included accuracy of curly arrows (Exemplar 7 below) and omission of HCl as product from the regeneration of the catalyst. The responses of lower ability candidates also contained errors in the equation for the formation of the electrophile. Such responses used chlorine rather than ethanoyl chloride.

Exemplar 6

Formation of electrophile $\text{CH}_3\text{COCl} + \text{AlCl}_3 \rightarrow \text{CH}_3\text{CO}^+ + \text{AlCl}_4^-$

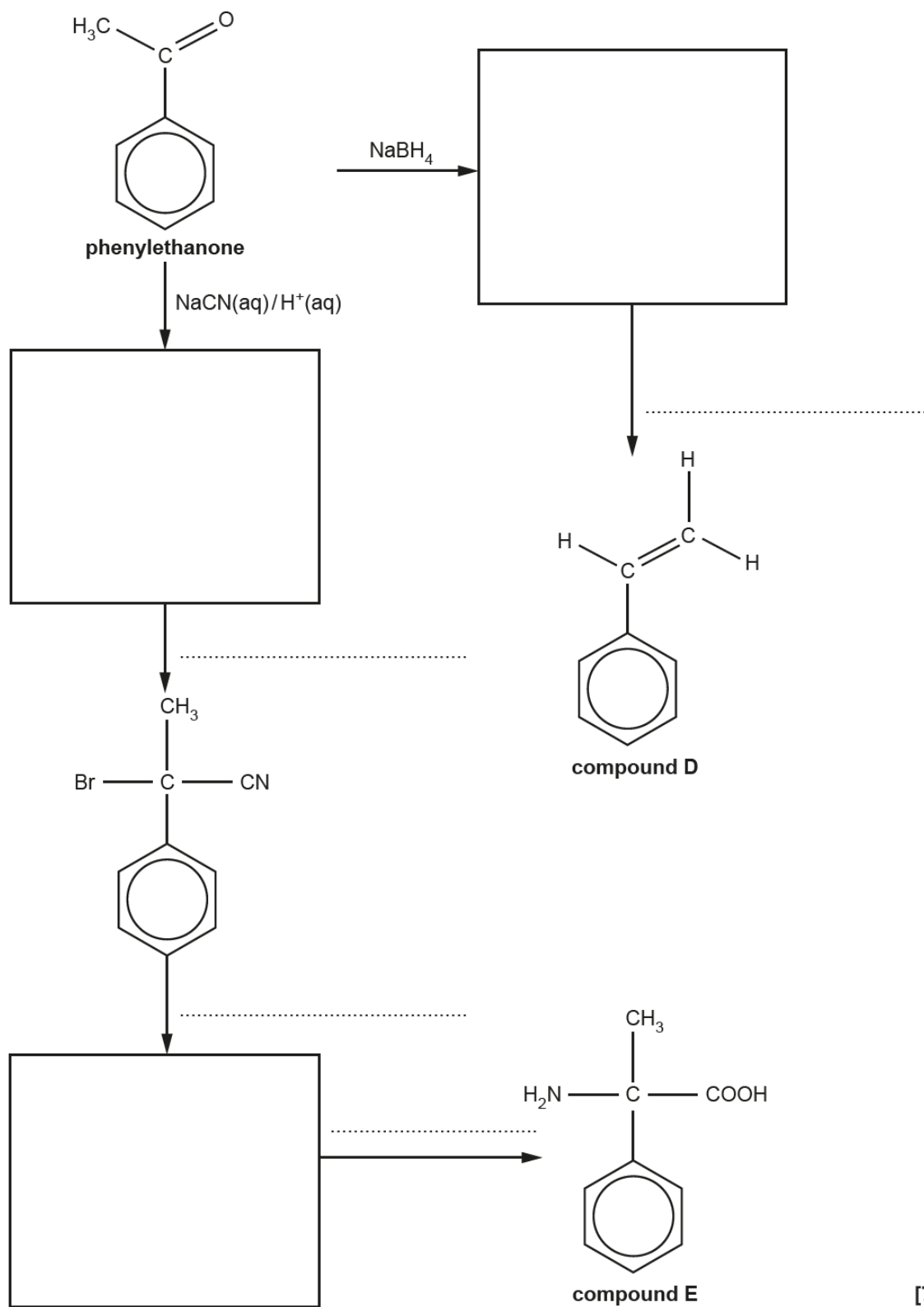


Regeneration of catalyst $\text{AlCl}_4^- + \text{H}^+ \rightarrow \text{AlCl}_3 + \text{HCl}$

This response demonstrates a near perfect attempt at this question. The equations for the formation of the electrophile and regeneration of the catalyst are correct. The first curly arrow is drawn accurately from the circle of the benzene ring to the correct carbon atom of the electrophile. The intermediate is correct, with the π ring over the five carbon atoms and in the correct orientation. Unfortunately the curly arrow drawn to reform the π bond starts at the H atom rather than from the bond. This small error has prevented this candidate from being given full marks.

Question 19 (b) (iv)

(iv) Complete the flowchart for the synthesis of compounds **D** and **E** from phenylethanone.

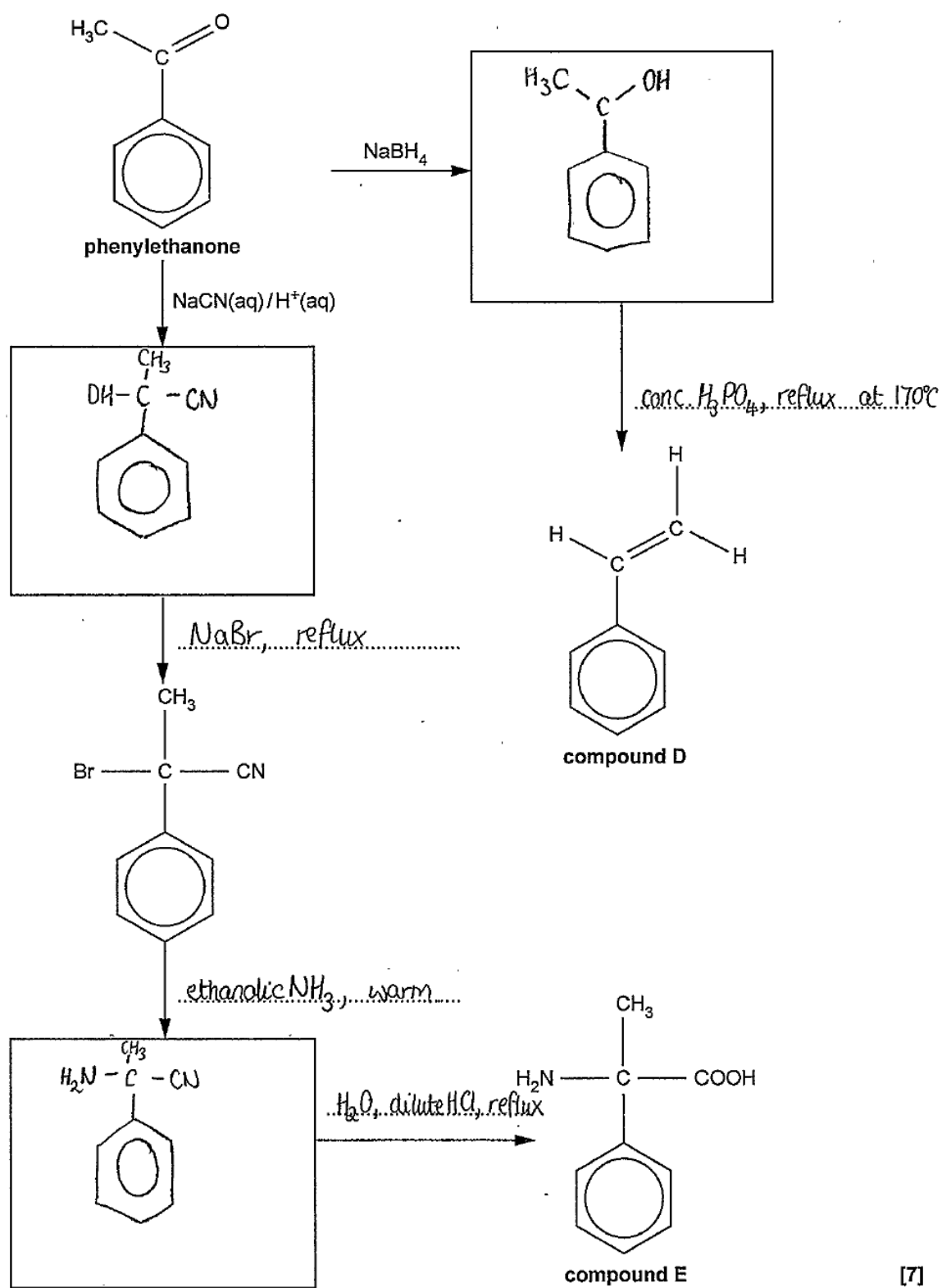


[7]

Turn over

This question required candidates to apply knowledge of organic reactions from across the specification and discriminated well. Candidates with a good knowledge of reagents and conditions frequently scored over five marks. More detailed feedback is discussed with Exemplar 7, below.

Exemplar 7



[7]

Phenylethanone is the starting point of this flowchart which shows the synthesis of compounds **D** and **E**.

Synthesis of **D**

The first step in the synthesis of **D** is the reduction of the ketone group. This response demonstrates a common error seen by examiners. The candidate has correctly deduced that an alcohol is formed but has omitted a hydrogen atom. Candidates are advised to take care when drawing structures. If a carbon atom is displayed it should be shown to be making four bonds. The final step of the synthesis is the dehydration of the alcohol with an acid. This candidate has used H_3PO_4 . H_2SO_4 was also frequently seen. Lower ability responses included reference to water or steam and this was not credited.

Synthesis of **E**

The first step of the synthesis of **E** from phenylethanone is the reaction with $\text{NaCN}(\text{aq})/\text{H}^+(\text{aq})$. This candidate identifies that the product of the reaction is a hydroxynitrile but unfortunately this cannot be credited due to the incorrect linking of the OH group via the H atom. Candidates should be aware that, when drawing structures, groups must be bonded via the correct atoms.

The next step of the synthesis is the substitution of the OH group. The candidate correctly recognises that NaBr is a suitable reagent but omits an acid, e.g. H_2SO_4 , which is also required for this reaction. This error was seen frequently by examiners.

The final two steps involve the substitution of the Br atom and acid hydrolysis of the nitrile group. In this case the candidate chooses the reaction with excess NH_3 . The structure of the correct product of this reaction is shown and the synthesis is completed by identifying a suitable reagent for the final step. Other candidates opted to perform these steps in the reverse order and the mark scheme allowed full credit for either approach.

Common errors in the final steps were omissions. Some candidates simply stated NH_3 without mentioning ethanol. Others identified water as important for the hydrolysis but did not include reference to an acid.

Question 20 (a) (i)

20 This question is about reaction mechanisms.

(a) Chemists use curly arrows in reaction mechanisms.

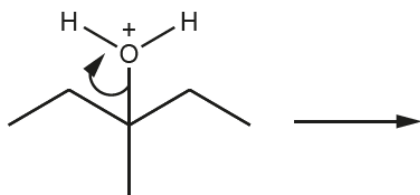
(i) What does a curly arrow show in a reaction mechanism?

.....
..... [1]

Most candidates were able to state that a curly arrow shows the movement of a pair of electrons. However, many candidates gave responses that lacked precision, such as 'movement of electrons'. Such responses did not receive credit as the number of electrons was not specified.

Question 20 (a) (ii)

(ii) Draw structures to show the products in the reaction mechanism below.



[2]

This demanding question required candidates to apply their knowledge of curly arrows to an unfamiliar intermediate. Examiners were impressed by the number of good responses and many candidates were able to draw an organic product with the correct carbon skeleton. The best responses demonstrated candidates' flair for the subject and these recognised that a carbocation would be formed rather than an alkane.

Question 20 (a) (iii)

(iii) Use the mechanism in (ii) to explain what is meant by **heterolytic fission**.

.....

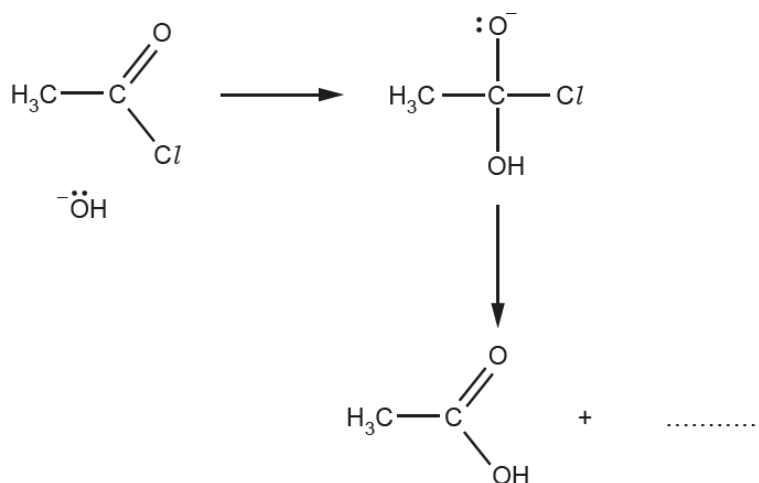
 [2]

Many candidates were able to describe the meaning of 'heterolytic', referring to both electrons going to the O atom. However, only some candidates described 'fission' and a significant proportion of these referred only to 'bond breaking'. The best responses correctly stated that fission is the breaking of a covalent bond. Candidates are encouraged to read questions carefully and take notice of words that appear in bold type as these often communicate what is expected in a question.

Question 20 (b) (i)

(b) An incomplete reaction mechanism is shown below.

(i) Complete the mechanism by adding curly arrows and any missing species.



[4]

Examiners were encouraged by the number of excellent responses to this question. Candidates were able to confidently apply their knowledge of mechanisms to this unfamiliar example and the majority of the cohort scored at least two marks. In the first step candidates used their understanding of nucleophilic addition to show a correct curly arrow from the hydroxide ion to the C of the C=O bond as well as an arrow from this bond to the O. Many candidates were able to show the breaking of the C–Cl bond and the formation of a chloride ion, drawing on their experience of the reactions of haloalkanes. Some candidates recognised the need to include an arrow to reform the carbon-oxygen double bond, with the best responses showing this accurately. A common error was to draw the bond from the lone pair on O to the C atom, rather than the bond.

Question 21

21* Analysis of an unknown organic compound produced the following results.

Elemental analysis by mass

C: 73.17%; H: 7.32%; O: 19.51%

Mass spectrum

Molecular ion peak at $m/z = 164.0$

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The numbers by the peaks are the relative peak areas.

Use the results to suggest **one** possible structure for the unknown compound.

Show **all** your reasoning.

[6]

Candidates are confident in tackling questions requiring spectral analysis. Most candidates were able to determine the empirical and molecular formula of the unknown compound and analyse the IR and NMR data. A number of excellent responses were seen which included interpretation of the peak splitting in the NMR spectrum. However, many candidates were unable to suggest a structure that matched their spectral analysis. The majority of structures seen were aromatic but not all contained the carboxylic acid group. Some candidates focused on the NMR data and suggested a structure that was consistent with some of these peaks and included a two substituents of the ring or a degree of chain branching. Lower ability responses often showed a simpler structure of a monosubstituted ring with a straight chain. Stronger responses were able to use all the data to suggest a correct structure as demonstrated in Exemplar 9. Examiners were impressed with the problem solving ability shown by candidates and a significant proportion of responses were given six marks.

Exemplar 8

$$\begin{array}{ccc}
 \text{C: } \frac{73}{12} & \text{H: } \frac{7.32}{1} & \text{O: } \frac{19.51}{16} \\
 = 6.0975 & = 7.32 & = 1.219375 \\
 \frac{6.0975}{1.219375} & \frac{7.32}{1.219375} & \frac{1.219375}{1.219375} \\
 = 5 & = 6 & = 1
 \end{array}$$

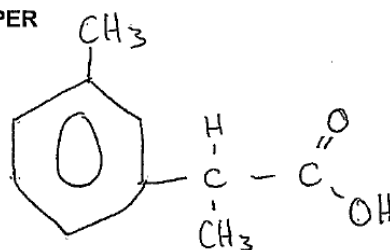
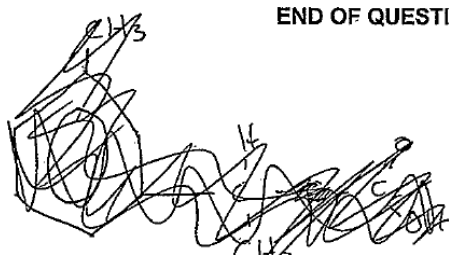
Empirical = $\text{C}_5\text{H}_6\text{O}$ The molecular mass is 164 so
the molecular formula is $\text{C}_{10}\text{H}_{12}\text{O}_2$

The sharp peak at 1700 cm^{-1} is due to a C=O group.
The broad peak at 3000 cm^{-1} is due to a O-H. This
suggests a carboxylic acid is present.

Additional answer space if required

Peak at 1.5 ppm is due to a CH_3 group. It is a doublet due
to being adjacent to 1 proton. Peak at 2.4 ppm is due to a
 $\text{O}-\text{CH}_3$ group. It is a singlet due to being adjacent to
0 protons. Peak at 7.2 ppm is due to a benzene
ring. The peak at 2.7 ppm is due to a
 $\text{HC}-\overset{\text{O}}{\parallel}{\text{C}}$ group. It is a quartet due to
being adjacent to 3 protons.

END OF QUESTION PAPER



This candidate starts their analysis by determining the empirical and molecular formula of the unknown compound. Next the IR and NMR data is analysed in a clear, logical fashion. Although not shown in this report, the candidate had annotated the spectra, a good strategy. At the end of the response the candidate has determined a possible structure. Notice how the candidate has crossed out the first attempt at a structure. This is much better than rubbing out a pencil diagram and re-drawing over the space as this often leads to unclear images that are difficult for examiners to read. This candidate received full marks in this question.

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