GCE A LEVEL

1410U40 – 1

TUESDAY, 18 JUNE 2024 – MORNING

CHEMISTRY – A2 UNIT 4
ORGANIC CHEMISTRY AND ANALYSIS

1 hour 45 minutes plus your additional time allowance

Surname: _____

First name(s): _____

Centre Number: _____

Candidate Number: 2 _____

	For Examiner's Use Only		
	Question	Maximum Mark	Mark Awarded
Section A	1. to 6.	10	
Section B	7.	14	
	8.	15	
	9.	15	
	10.	12	
	11.	14	
	Total	80	

ADDITIONAL MATERIALS

A calculator and ruler

DATA BOOKLET supplied by WJEC

ITEMS INCLUDED WITH QUESTION PAPER

A separate Diagram Booklet.

The Diagram Booklet MUST be handed in to the invigilators and sent for marking.

INSTRUCTIONS TO CANDIDATES

Use black ink, black ball–point pen, black felt tip or your usual method.

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

SECTION A Answer ALL questions.

SECTION B Answer ALL questions.

Write your answers in the spaces provided. If you run out of space, use the additional pages at the back of this booklet, taking care to number the question(s) correctly.

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 Q10 (a).

SECTION A

Answer ALL questions.

1. Phenylmethyl ethanoate, used in perfumery, is made by reacting phenylmethanol and ethanoyl chloride.

Refer to the equation for Question 1 in the separate Diagram Booklet. Complete the equation for this reaction, showing the structure of the organic product.

[1 mark]

2. An azo dye has a maximum absorption of visible light at 403 nm.

(a) Calculate the frequency corresponding to this wavelength.

Frequency = _____ Hz

[1 mark]

continued on the next page . . .

Question 2 continued

2. (b) Explain why this dye is yellow in white light.

_____

_____

_____

[1 mark]

3. Refer to the diagram for Question 3 in the separate Diagram Booklet. Four isomers of formula $C_6H_{12}O_2$ are shown in the diagram.

Deduce which isomer has an infrared absorption spectrum showing absorptions at $1620\ cm^{-1}$ and at $3200 – 3500\ cm^{-1}$ but NOT at $1650 – 1750\ cm^{-1}$

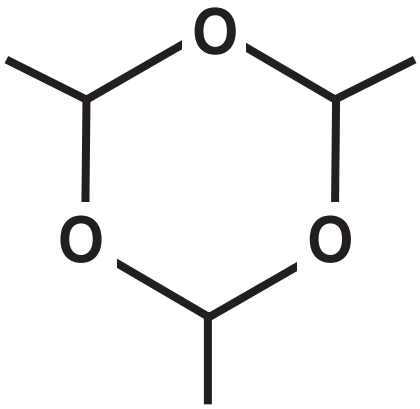
Give reasons for your answer.

[2 marks]

4. Give the formula of the triphenylmethyl radical.

[1 mark]

5. The structure of paraldehyde is shown below.



Explain what would be seen in the ^{13}C NMR spectrum of this compound.

References to the positions of the chemical shifts are NOT required.

[2 marks]

6. **Refer to the diagram for Question 6 in the separate Diagram Booklet. Ethanal is oxidised by selenium dioxide giving ethanedial.**
The equation for this reaction is shown in the diagram.

Calculate the atom economy of this reaction to produce ethanedial.

Give your answer to an APPROPRIATE number of significant figures.

Atom economy = _____ %

[2 marks]

(Total for SECTION A = 10 marks)

SECTION B

Answer ALL questions.

7. (a) Nitrobenzene can be made by the nitration of benzene.

(i) State the reagent(s) used for this reaction.

_____

_____

[1 mark]

(ii) State the FORMULA of the nitrogen – containing electrophile that takes part in this reaction.

_____

[1 mark]

continued on the next page . . .

Question 7 continued

7. (b) Aromatic nitro – compounds are useful in synthesis as they are often the starting materials for producing other compounds.

Refer to the diagram for Question 7 (b) in the separate Diagram Booklet. Study the reaction sequence shown in the diagram and then answer the questions that follow.

(i) State the type of reaction occurring during stage 1

_____

[1 mark]

(ii) State the reagent(s) used in stage 2

_____

[1 mark]

(iii) State the reagent(s) used to produce benzene – 1,4 – diol in stage 3

_____

[1 mark]

continued on the next page . . .

Question 7 (b) continued

7. (b) (iv) State the colour change undergone by the reagents in stage 4

_____

[1 mark]

(v) The reaction product in stage 4, cyclohexadiene–1,4–dione acts as an alkene.

I. State the type of reaction mechanism that occurs when an alkene reacts with bromine.

_____

[1 mark]

continued on the next page . . .

Question 7 (b) (v) continued

7. (b) (v) II. Draw the structure of the compound obtained when 1 mol of cyclohexadiene – 1,4 – dione reacts with 2 mol of bromine.

[1 mark]

continued on the next page . . .

Question 7 continued

7. (c) Refer to the diagram for Question 7 (c) (i) in the separate Diagram Booklet. Methyl orange is a water soluble acid – base indicator. The structure of this compound is shown in the diagram.

(i) Give the structure of the starting sulfur – containing compound that is coupled with N,N – dimethylphenylamine to give methyl orange.

[1 mark]

continued on the next page . . .

Question 7 (c) continued

7. (c) (ii) Refer to the diagram for Question 7 (c) (ii) in the separate Diagram Booklet. Suggest why, in basic solution, methyl orange exists as the species shown in the diagram.

_____

_____

_____

[1 mark]

(d) Refer to the diagram for Question 7 (d) in the separate Diagram Booklet. Compound J is present in relatively large quantities in red peppers.

Study the diagram and then answer the questions that follow.

continued on the next page . . .

Question 7 (d) continued

7. (d) (i) State what is seen when compound J reacts with iron(III) chloride solution.

_____

[1 mark]

(ii) State what is seen when compound J reacts with sodium hydrogencarbonate solution.

_____

[1 mark]

(iii) Give the structure of the compound formed when compound J reacts with hydrogen bromide.

[1 mark]

continued on the next page . . .

Question 7 (d) continued

7. (d) (iv) Give the structure of the compound formed when compound J reacts with ethanoyl chloride.

[1 mark]

(Total for Question 7 = 14 marks)

8. (a) Refer to the diagram for Question 8 (a) (i) in the separate Diagram Booklet. Compound **M** is an aliphatic compound, which contains two bromine atoms.

(i) Compound **M** reacts with an excess of alcoholic potassium hydroxide solution to give compound **N**, which has the formula **R — C ≡ C — R'.**

Suggest the role of the alcoholic potassium hydroxide in this elimination reaction.

_____

[1 mark]

(ii) Refer to the diagram for Question 8 (a) (ii) in the separate Diagram Booklet. Compound **M** reacts with aqueous sodium hydroxide to give compound **P**.

State the type of reaction mechanism occurring.

_____

[1 mark]

continued on the next page . . .

Question 8 (a) continued

8. (a) (iii) Refer to the diagram for Question 8 (a) (iii) in the separate Diagram Booklet. Compound P can undergo bond fission when it is heated with a suitable oxidising agent to form two aldehydes S and T.

The mass spectrum of compound S showed a molecular ion at m/z 72

I. The mass spectrum of compound S showed that the alkyl group R was branched.

Deduce the structure of compound S. Show your reasoning.

[2 marks]

continued on the next page . . .

Question 8 (a) (iii) continued

8. (a) (iii) II. Compounds S and T both reacted with 2,4 – dinitrophenylhydrazine to give solid derivatives.

State the colour of these derivatives.

[1 mark]

III. The melting temperatures of the derivatives of compounds S and T in part II above are shown in the table below.

Compound	Melting temperature (°C)
S	185 – 187
T	186 – 189

continued on the next page . . .

Question 8 (a) (iii) III continued

Describe how the melting temperature of a 50:50 mixture of the two derivatives differs from those shown in the table.

_____

_____

_____

[1 mark]

continued on the next page . . .

Question 8 continued

8. (b) Refer to the diagram for Question 8 (b) in the separate Diagram Booklet. Pinacolone is prepared from a diol containing 6 carbon atoms.

After the reaction, flammable pinacolone is distilled from the reaction mixture. The distillate consists of two layers – an aqueous layer and a less dense layer containing mainly pinacolone.

(i) Describe how you would separate these two layers.

_____

_____

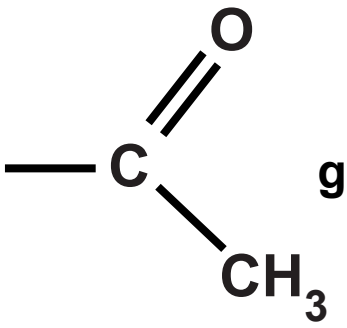
_____

[1 mark]

continued on the next page . . .

Question 8 (b) continued

8. (b) (ii) Describe a chemical test, giving reagent(s) and observations, to show that

pinacolone contains a  **group.**

[2 marks]

continued on the next page . . .

Question 8 (b) continued

8. (b) (iii) Refer back to the diagram for Question 8 (b) in the separate Diagram Booklet. The high resolution ^{1}H NMR spectrum of pinacolone consists of two signals.

Complete the table below that describes these two signals.

Protons	Splitting pattern	Relative peak area
CH_3CO		
$(CH_3)_3C$		

[2 marks]

continued on the next page . . .

Question 8 (b) continued

8. (b) (iv) Refer to the diagram for Question 8 (b) (iv) in the separate Diagram Booklet. Under suitable conditions pinacolone was reduced, giving a mixture of

2,2–dimethylbutane and

3,3–dimethylbutan–2–ol together with some unreacted pinacolone.

The three compounds shown in the diagram were separated by gas chromatography.

I. Mary said that the boiling temperature of 3,3–dimethylbutan–2–ol would be the highest of these three compounds and that this could be used to identify it.

Explain why she is correct.

[2 marks]

8. (b) (iv) II. The ^{13}C NMR spectra of the remaining two compounds were taken.

Suggest how the ^{13}C NMR spectra of these two compounds would be similar and how they would be different.

Similar

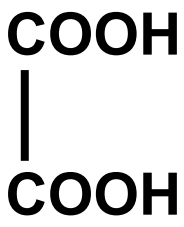
Different

[2 marks]

(Total for Question 8 = 15 marks)

9. (a) Ethanedioic acid is an important industrial chemical.

ethanedioic acid



One method for its manufacture is by the reaction of butan–1–ol, carbon monoxide and oxygen at a pressure of 10 MPa and at a temperature of 100 °C in the liquid phase. The process uses a catalyst of palladium mounted on graphite.

The first stage gives the ester di–1–butyl ethanedioate, which is then hydrolysed to give ethanedioic acid and butan–1–ol.

continued on the next page . . .

Question 9 (a) continued

9. (a) (i) Refer to the diagram for Question 9 (a) (i) in the separate Diagram Booklet. Balance the equation for the first stage of this process.

[1 mark]

(ii) Suggest ONE reason why this stage of the process may be seen as relatively uneconomic.

_____

_____

_____

[1 mark]

continued on the next page . . .

Question 9 (a) continued

9. (a) (iii) Hydrolysis of the ester gives ethanedioic acid and butan–1–ol.

Explain why ethanedioic acid is soluble in water but di–1–butyl ethanedioate is virtually insoluble in water. Include a diagram in your answer.

[3 marks]

continued on the next page . . .

Question 9 continued

9. (b) Refer to the diagram for Question 9 (b) in the separate Diagram Booklet. An older method for manufacturing ethanedioic acid produces insoluble calcium ethanedioate (M_r 128) as an intermediate. This is reacted with aqueous sulfuric acid to produce calcium sulfate and an aqueous solution of ethanedioic acid.

Ethanedioic acid crystallises as its dihydrate.

In a laboratory experiment 11•52 g of calcium ethanedioate was reacted with aqueous sulfuric acid of concentration 2•00 mol dm^{-3}

continued on the next page . . .

Question 9 (b) continued

9. (b) (i) Calculate the minimum volume of this aqueous sulfuric acid needed to just react with all the calcium ethanedioate.

Minimum volume = _____ cm^3

[2 marks]

continued on the next page . . .

Question 9 (b) continued

9. (b) (ii) After removal of insoluble calcium sulfate, the residue was washed with water. The solution was boiled until 50•0 cm^3 (50•0 g) of solution remained. The solubility of ethanedioic acid dihydrate, $(COOH)_2.2H_2O$ (M_r 126) is 14•3 g / 100 g of solution at 20 °C.

Calculate the mass of ethanedioic acid dihydrate that crystallised from this solution at 20 °C.

Mass = _____ g

[3 marks]

continued on the next page . . .

Question 9 continued

9. (c) The removal of alkyl fluorocarbons and CFCs from the environment presents a difficult problem.

One suggestion is to heat these halogenoalkanes with sodium ethanedioate. For example, difluoromethane reacts with sodium ethanedioate, $(COO)_2Na_2$, to give hexafluorobenzene, sodium carbonate (Na_2CO_3) and water.

Write an equation for this reaction on the page for Question 9 (c) in the separate Diagram Booklet.

[2 marks]

continued on the next page . . .

Question 9 continued

9. (d) Refer to the graph for Question 9 (d) in the separate Diagram Booklet. On heating, barium ethanedioate undergoes decomposition.

Use the graph to show that the equation for this reaction is:

$$(COO)_2Ba(s) \longrightarrow BaCO_3(s) + CO(g)$$

M_r 225 M_r 197

[2 marks]

continued on the next page . . .

Question 9 continued

9. (e) Decarboxylation occurs when carboxylic acids are heated with sodalime.

State the name of the organic compound produced when 4–ethylbenzenecarboxylic acid is heated with sodalime.

_____

[1 mark]

(Total for Question 9 = 15 marks)

10. (a) Refer to the diagram for Question 10 (a) in the separate Diagram Booklet. Compound **B** contains only carbon, hydrogen and bromine. The hydrogen and bromine atoms could be at any of the positions indicated by a circle in the structure shown.

- **5·35 g** of compound **B** contains **3·74 g** of bromine and **0·11 g** of hydrogen
- It rotates the plane of plane polarised light
- When **4·36 g** of compound **B** is heated with aqueous sodium hydroxide, the bromide ions produced react with silver ions to give **4·77 g** of silver bromide (M_r 187·9)

Use ALL of this information to deduce a possible structure for compound **B**.

Explain your reasoning.

[6 QER marks]

continued on the next page . . .

Question 10 continued

10. (b) Refer to the diagram for Question 10 (b) in the separate Diagram Booklet. Sucrose, $C_{12}H_{22}O_{11}$, is a sugar that contains eight —OH groups in each molecule. It reacts with ethanoic anhydride to give sucrose octaethanoate.

The diagram shows the word equation for this reaction.

(i) A 0•0700 mol sample of sucrose was used in a preparation.

Calculate the minimum volume of ethanoic anhydride needed to react with all the —OH groups present in this sample of sucrose.
Use the values in the table below.

ethanoic anhydride	M_r	Density (g cm^{-3})
	102	1•08

Answer space continues on the next page.

Question 10 (b) (i) continued

Minimum volume = _____ cm^3

[2 marks]

10. (b) (ii) There is interest in producing materials by 'green' methods.

Two methods are proposed for making sucrose octaethanoate in the laboratory.

Method X Refluxing the mixture at 139 °C using an electric hotplate

Method Y Ultrasonic irradiation at room temperature

continued on the next page . . .

Question 10 (b) (ii) continued

Apart from temperature, suggest TWO factors that should be considered when deciding which of these two methods is 'greener'.

1. _____

_____

_____

2. _____

_____

_____

[2 marks]

continued on the next page . . .

Question 10 continued

10. (c) Lactose is a reducing sugar and reacts with Fehling's reagent.

(i) State what is seen when lactose reacts with the dark blue solution of Fehling's reagent.

_____

[1 mark]

(ii) State which functional group must be present in a molecule of lactose for this result with Fehling's reagent.

_____

[1 mark]

(Total for Question 10 = 12 marks)

11. (a) Refer to the diagram for Question 11 (a) in the separate Diagram Booklet. The diagram shows a method to produce the polyamide W, starting from adipamide.

(i) Refer to the diagram for Question 11 (a) (i) in the separate Diagram Booklet. In the first stage adipamide is hydrolysed using aqueous sodium hydroxide, giving disodium hexanedioate as one of the products.

Complete and balance the equation for this stage.

[2 marks]

continued on the next page . . .

Question 11 (a) continued

11. (a) (ii) **Refer to the diagram for Question 11 (a) (ii) in the separate Diagram Booklet. In another stage, adipamide is reacted with bromine in the presence of alkali to give butane–1,4–diamine, $H_2N(CH_2)_4NH_2$**

In this stage 0•075 mol of adipamide was used. If the percentage yield of the diamine was 60%, calculate the mass of butane–1,4–diamine produced.

Mass = _____ g

[2 marks]

continued on the next page . . .

Question 11 (a) continued

11. (a) (iii) Refer to the diagram for Question 11 (a) (iii) in the separate Diagram Booklet. The sodium salt of hexanedioic acid produced in part (i) is then acidified and the hexanedioic acid produced is reacted with butane–1, 4–diamine to give polyamide W.

Polyamides contain a peptide link.

Show the peptide link present in the polyamide ON THE DIAGRAM.

[1 mark]

continued on the next page . . .

Question 11 (a) continued

11. (a) (iv) Refer to the diagram for Question 11 (a) (iv) in the separate Diagram Booklet.
An alternative method for producing hexanedioic acid is to treat adipamide with nitric(III) acid.

I. Give ONE advantage of the method using nitric(III) acid.

_____

_____

_____

[1 mark]

II. Suggest how you would know that this alternative reaction using nitric(III) acid is complete.

_____

_____

[1 mark]

continued on the next page . . .

Question 11 continued

11. (b) Refer to the diagram for Question 11 (b) in the separate Diagram Booklet. A tripeptide is formed from three different amino acids.

Its formula (shown as a zwitterion) is shown in the diagram.

(i) State why the formation of a peptide from amino acids is called a condensation reaction.

_____

_____

[1 mark]

continued on the next page . . .

Question 11 (b) continued

11. (b) (ii) Write the formula of the species formed from phenylalanine in acid solution.

[1 mark]

continued on the next page . . .

Question 11 (b) continued

11. (b) (iii) Refer to the diagram for Question 11 (b) (iii) in the separate Diagram Booklet.
The tripeptide is hydrolysed to give its amino acid fragments. A solution containing these three amino acids is separated using thin layer chromatography.

Use the blank chromatogram to show the position of the 'spot' given by alanine, which has an R_f value of $0 \cdot 54$
Show how you arrived at your answer.

[2 marks]

continued on the next page . . .

Question 11 continued

11. (c) A solution contains a mass of z g of ONE of the two enantiomers of alanine. It rotates the plane of plane polarised light in the clockwise direction (+) by $6°$ $(+6°)$.

The other enantiomer rotates the plane of plane polarised light in the anticlockwise direction (−).

Another solution contains the same total mass z g of a MIXTURE of both enantiomers. This mixture rotates the plane of plane polarised light by $1 \cdot 5°$ in the anticlockwise direction $(-1 \cdot 5°)$.

continued on the next page . . .

Question 11 (c) continued

Refer to the grid for Question 11 (c) in the separate Diagram Booklet. Use the information to plot a graph to show how the rotation changes with the percentage of the (−) enantiomer. Hence determine the percentages of the (+) and (−) enantiomers in the mixture.

Percentage of (+) enantiomer _____ %

Percentage of (−) enantiomer _____ %

[3 marks]

(Total for Question 11 = 14 marks)

TOTAL FOR SECTION B = 70 MARKS

END OF PAPER

TOTAL FOR PAPER = 80 MARKS

Question Number	Additional pages, if required. Write the question number(s) in the left – hand margin.

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GCE A LEVEL

1410U40–1

TUESDAY, 18 JUNE 2024 – MORNING

CHEMISTRY – A2 UNIT 4
ORGANIC CHEMISTRY AND ANALYSIS

The Diagram Booklet MUST be handed in to the invigilators and sent for marking.

Diagram Booklet

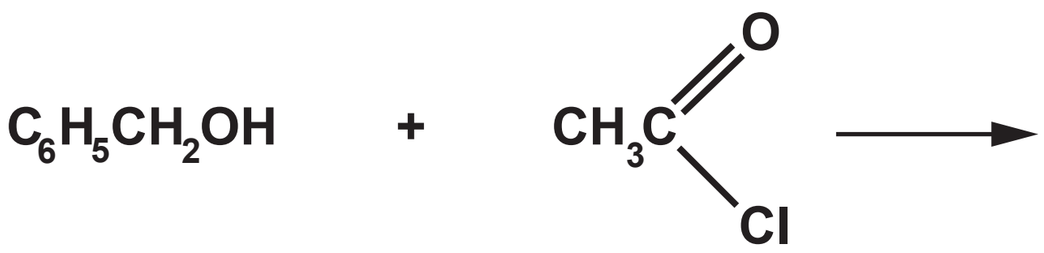
Surname: _____

First name(s): _____

Centre Number: _____

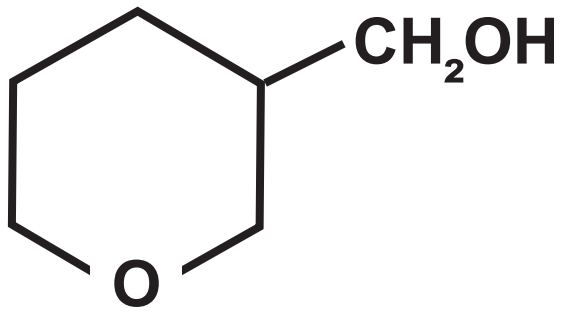
Candidate Number: 2 _____

Question 1

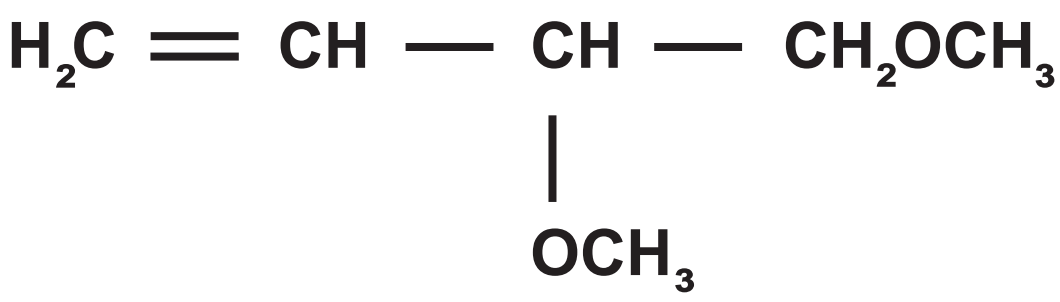


Question 3

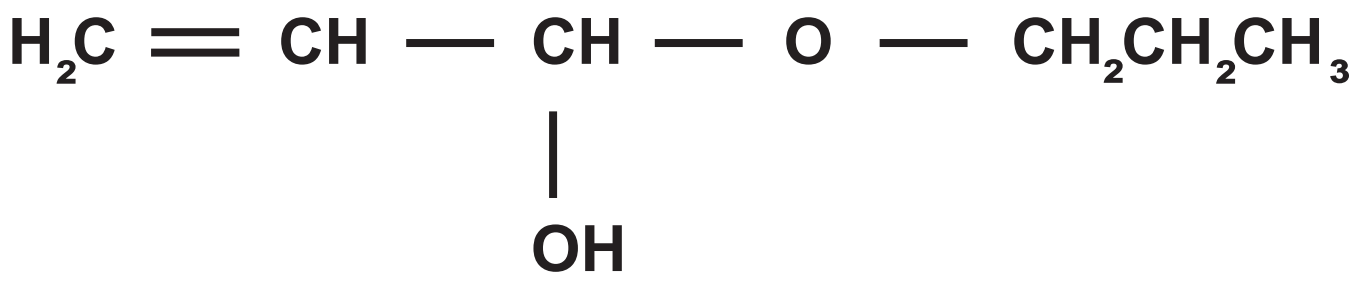
compound D



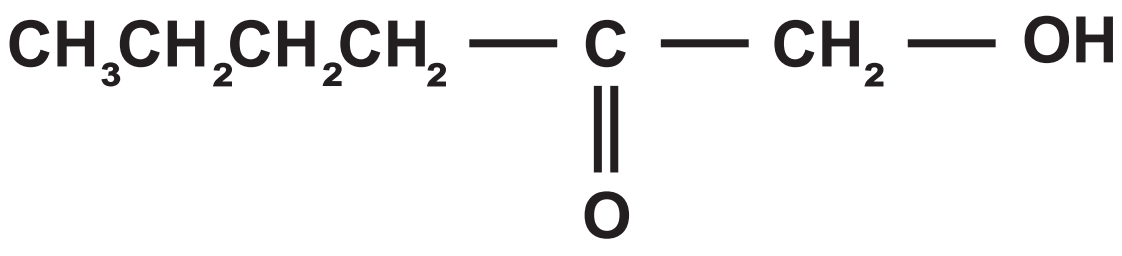
compound E



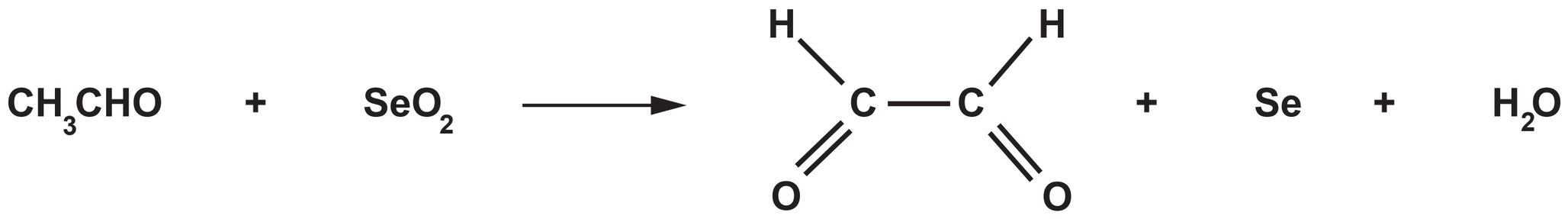
compound F



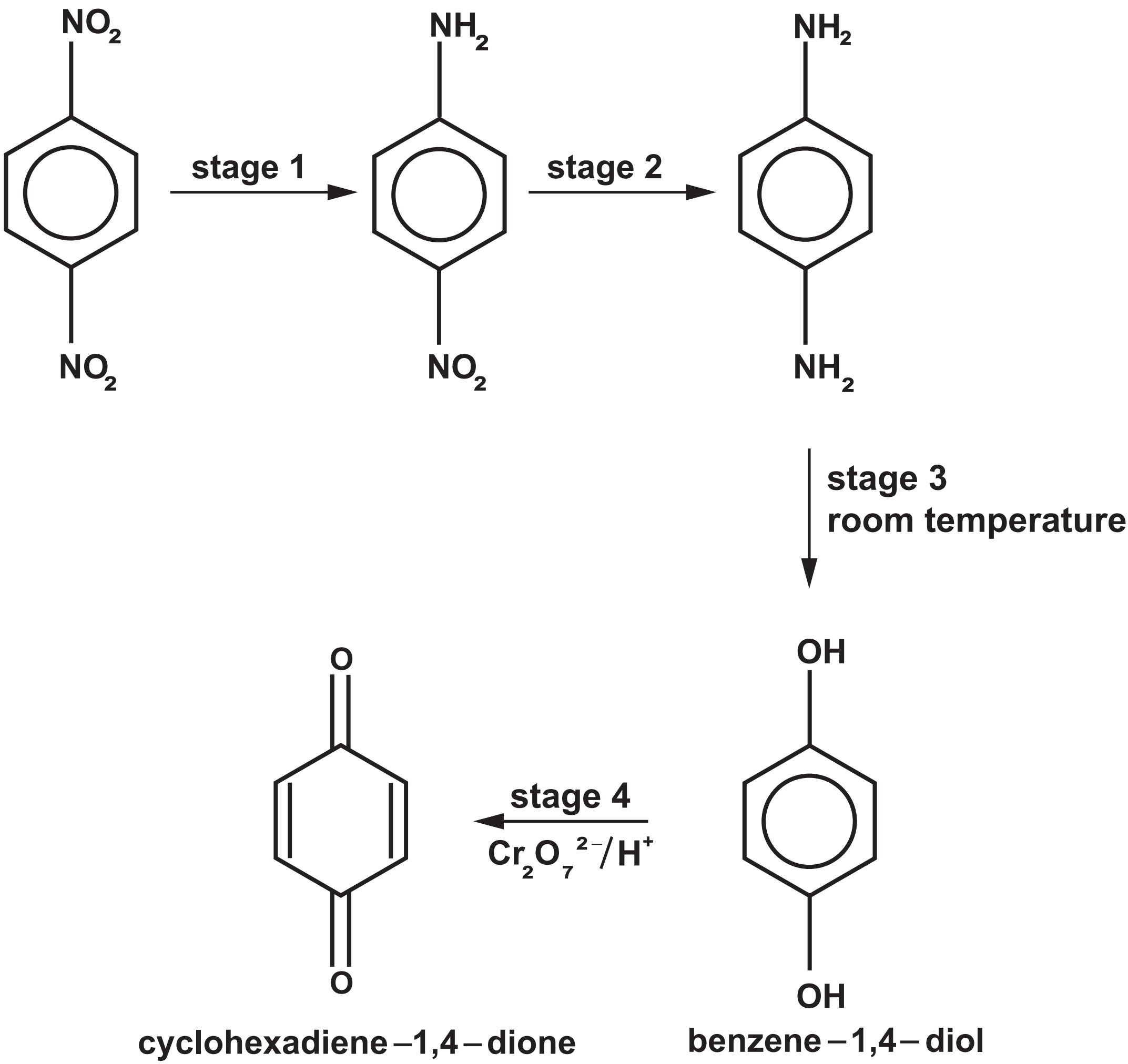
compound G



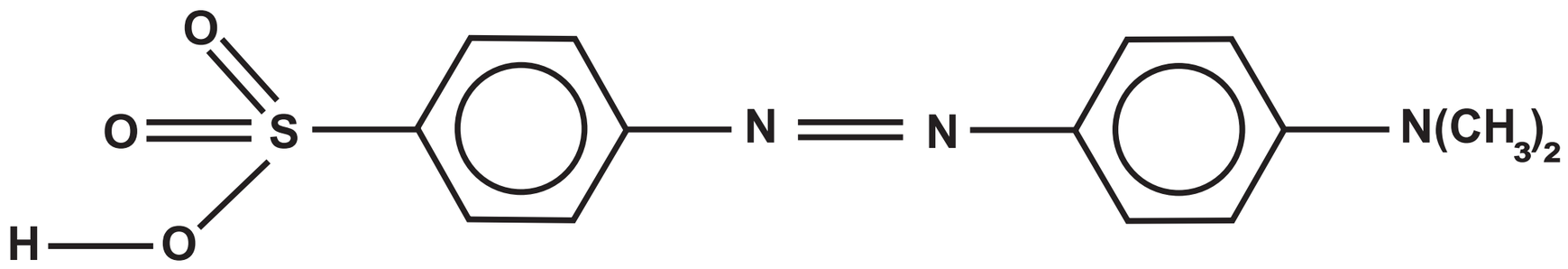
Question 6



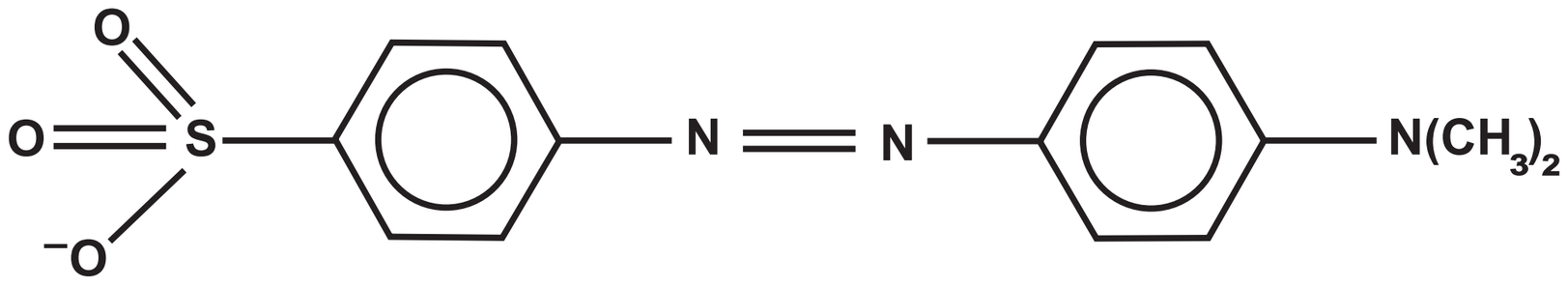
Question 7 (b)


NO2
stage 1
NH2
stage 2
NH2
NO2
NO2
NH2
stage 3
room temperature
O
stage 4
Cr2O7 2−/H+
OH
O
OH
cyclohexadiene –1,4 – dione
benzene – 1,4 – diol

Question 7 (c) (i)

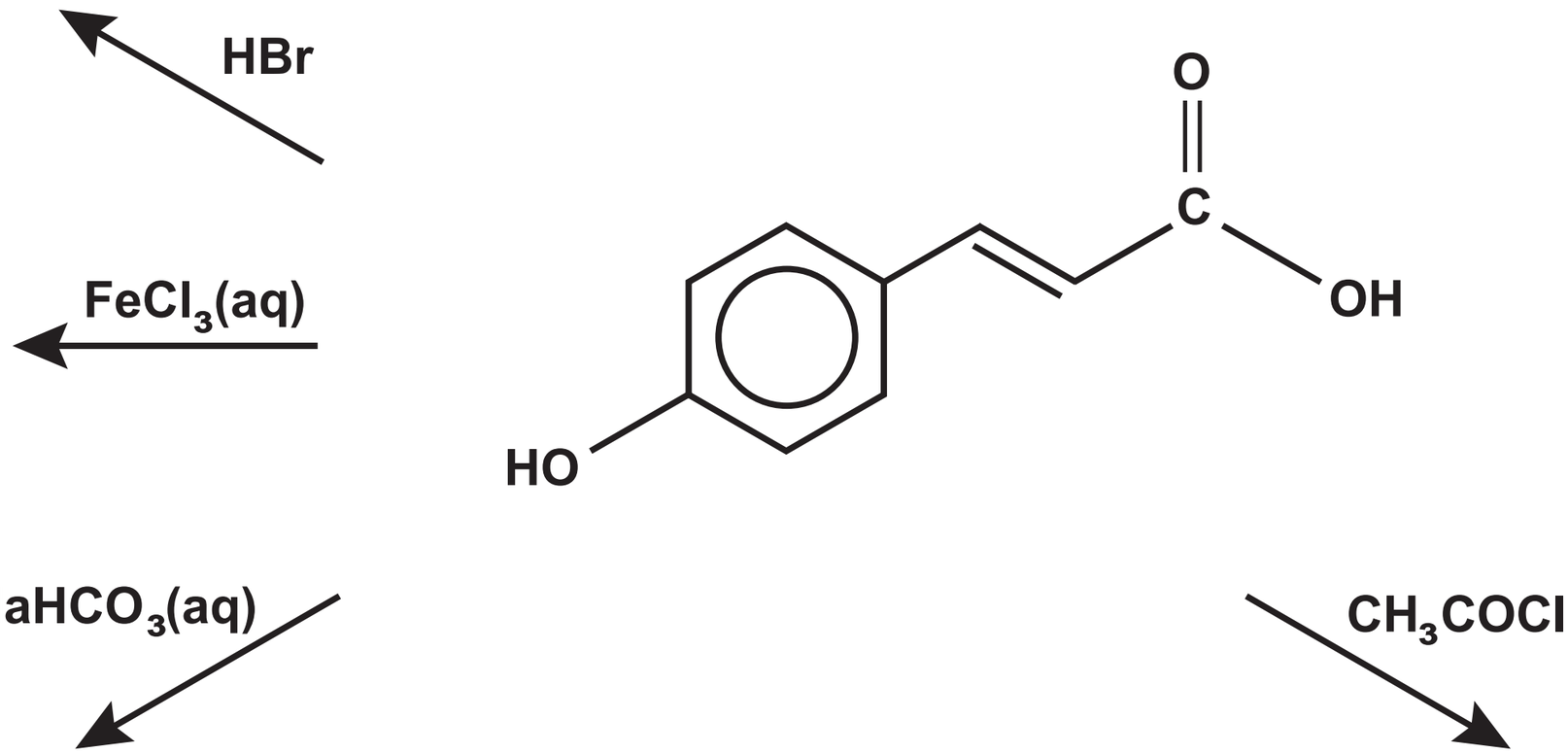


Question 7 (c) (ii)



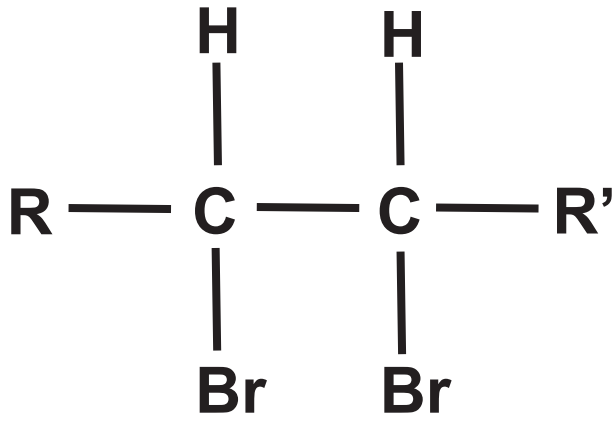
Question 7 (d)

compound J



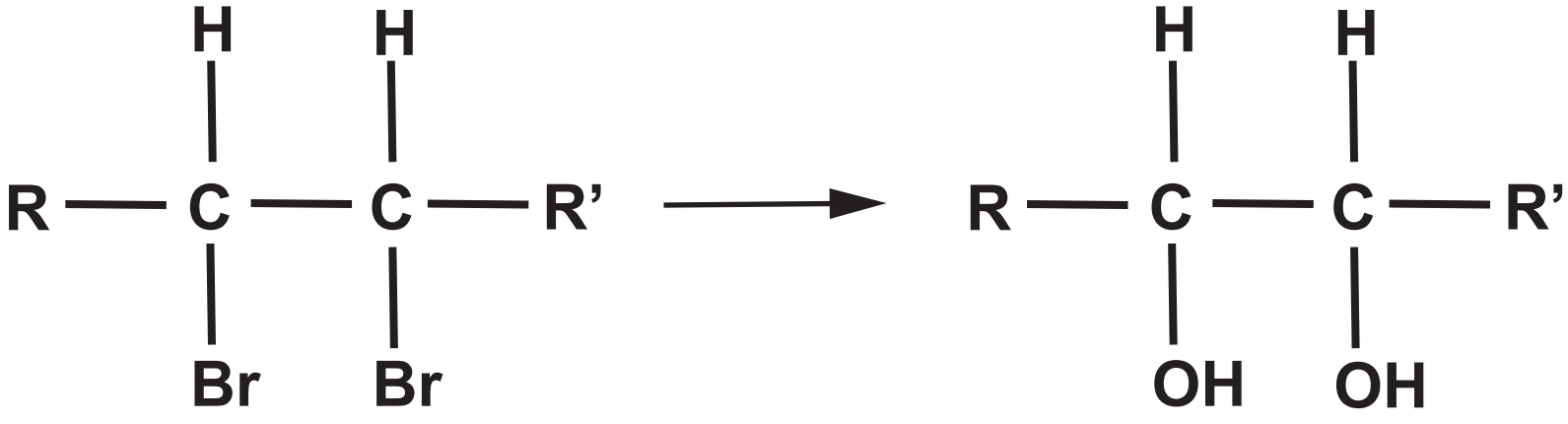
Question 8 (a) (i)

compound M



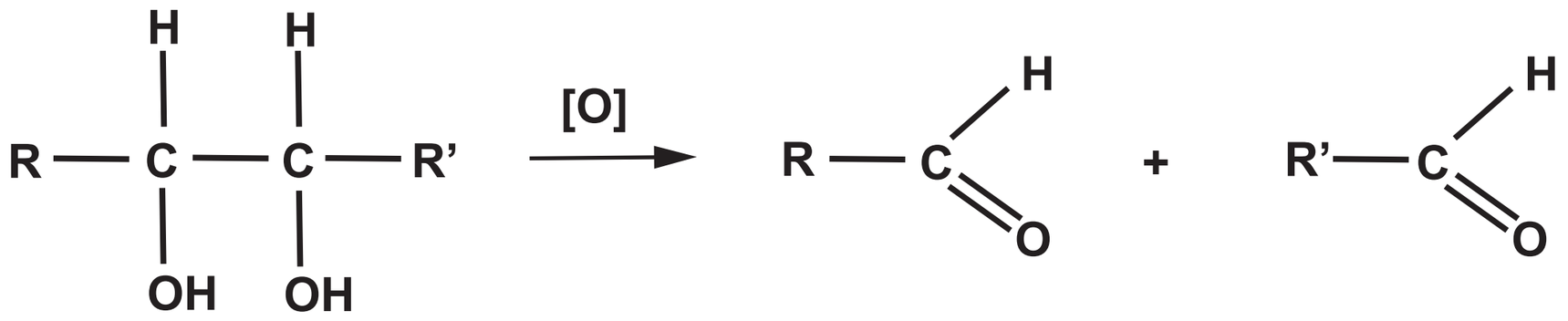
Question 8 (a) (ii)

compound **P**



Question 8 (a) (iii)

compound P **compound S** **compound T**

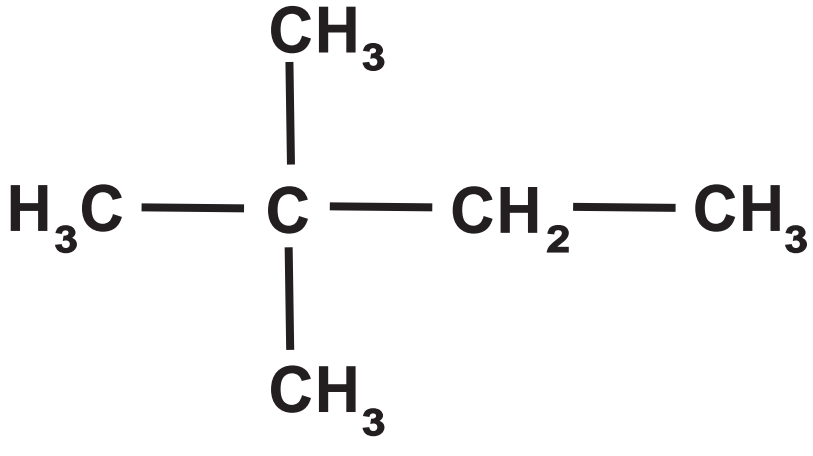


Question 8 (b)

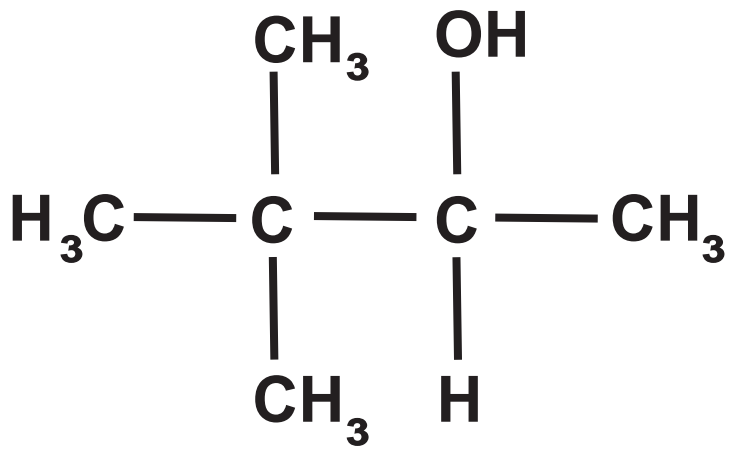
pinacolone

Question 8 (b) (iv)

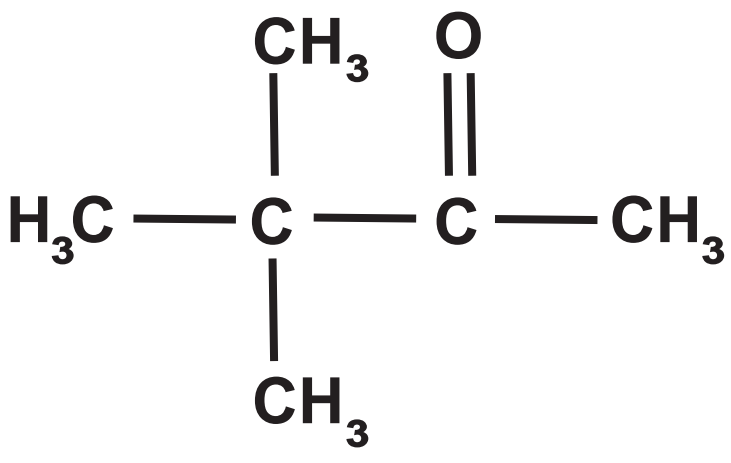
2,2–dimethylbutane



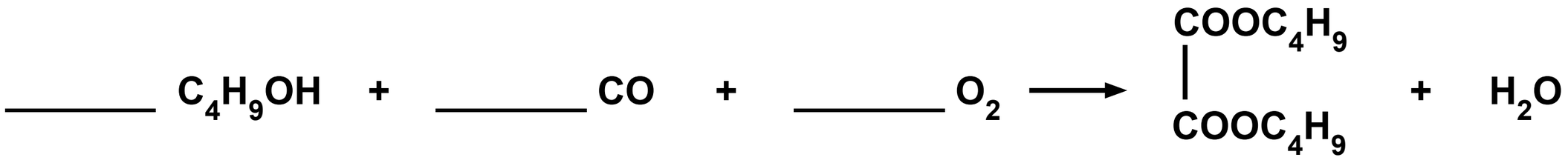
3,3–dimethylbutan–2–ol



pinacolone



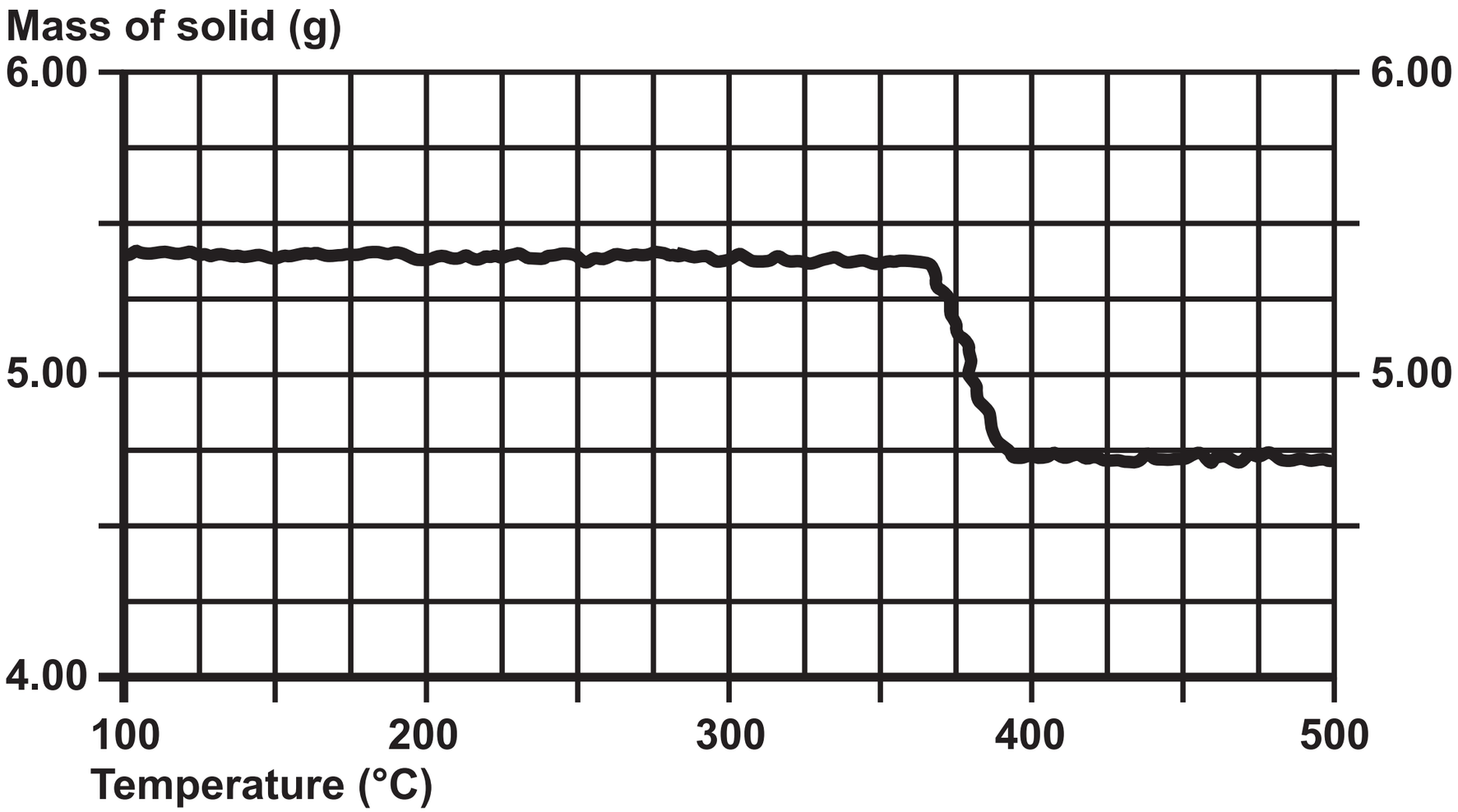
Question 9 (a) (i)



Question 9 (b)

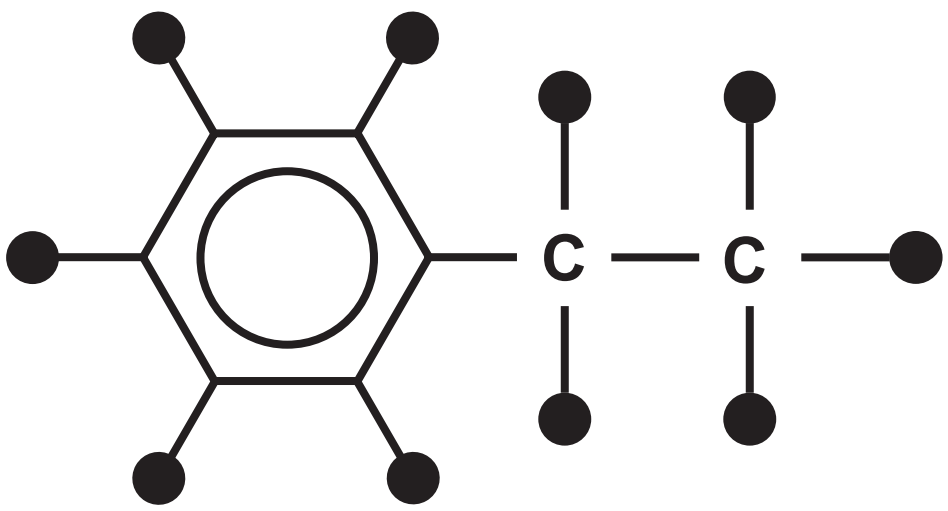
Question 9 (c)

Question 9 (d)


Mass of solid (g)
6.00
5.00
4.00
6.00
5.00
100
200
300
400
500
Temperature (°C)

Question 10 (a)

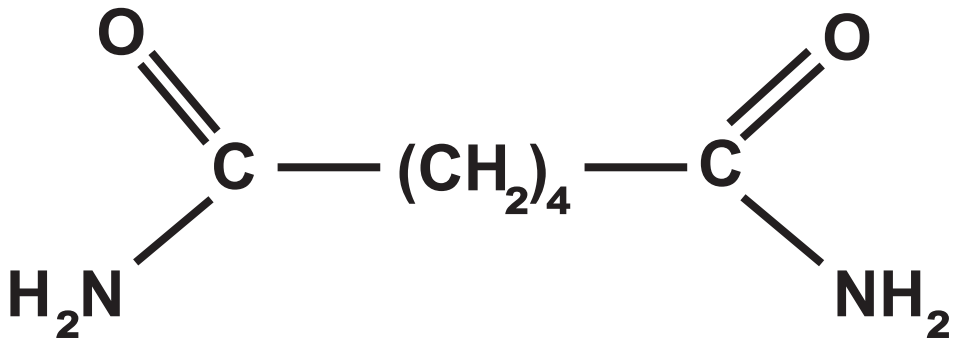
compound B



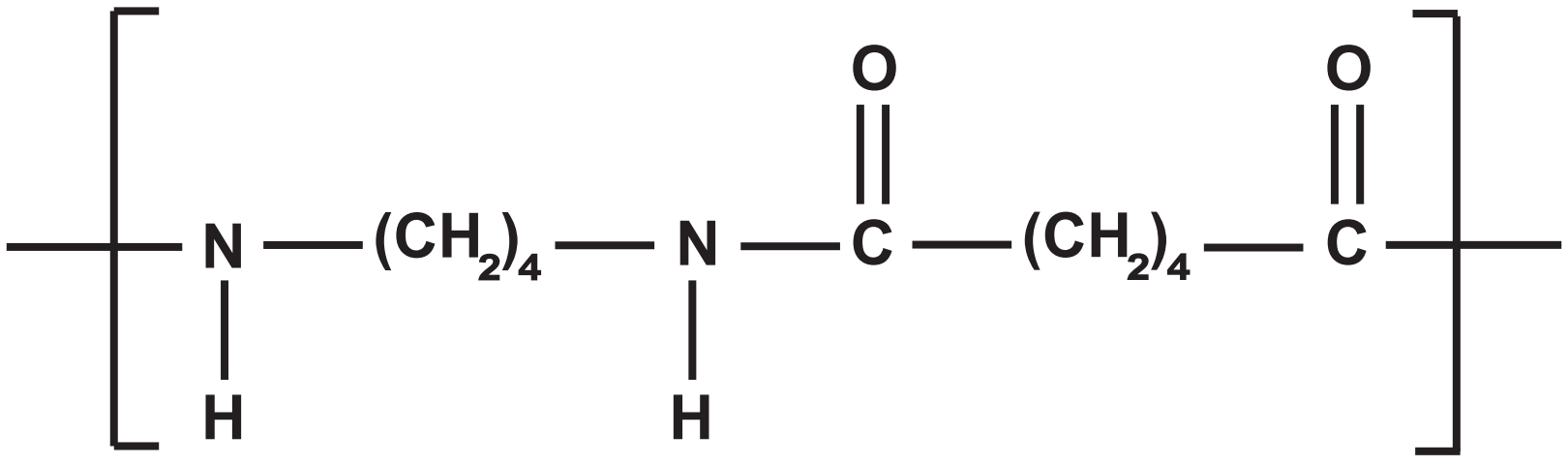
Question 10 (b)

Question 11 (a)

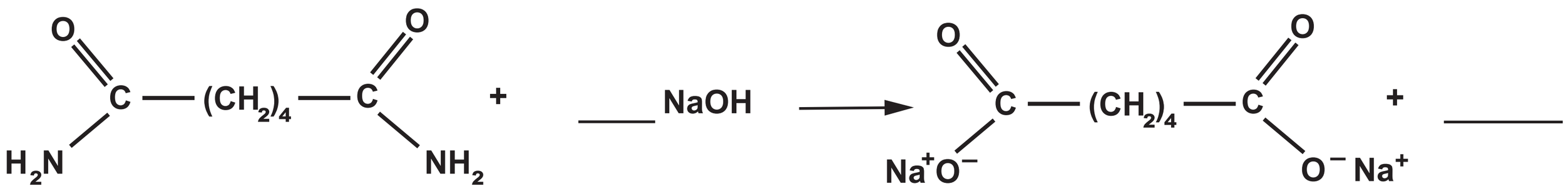
adipamide



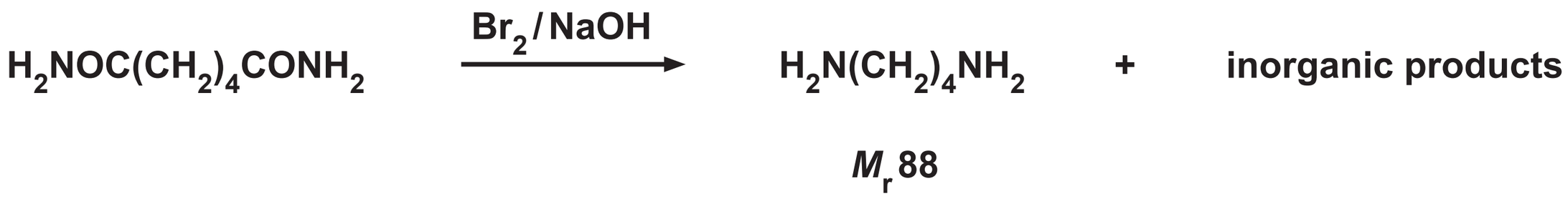
polyamide W



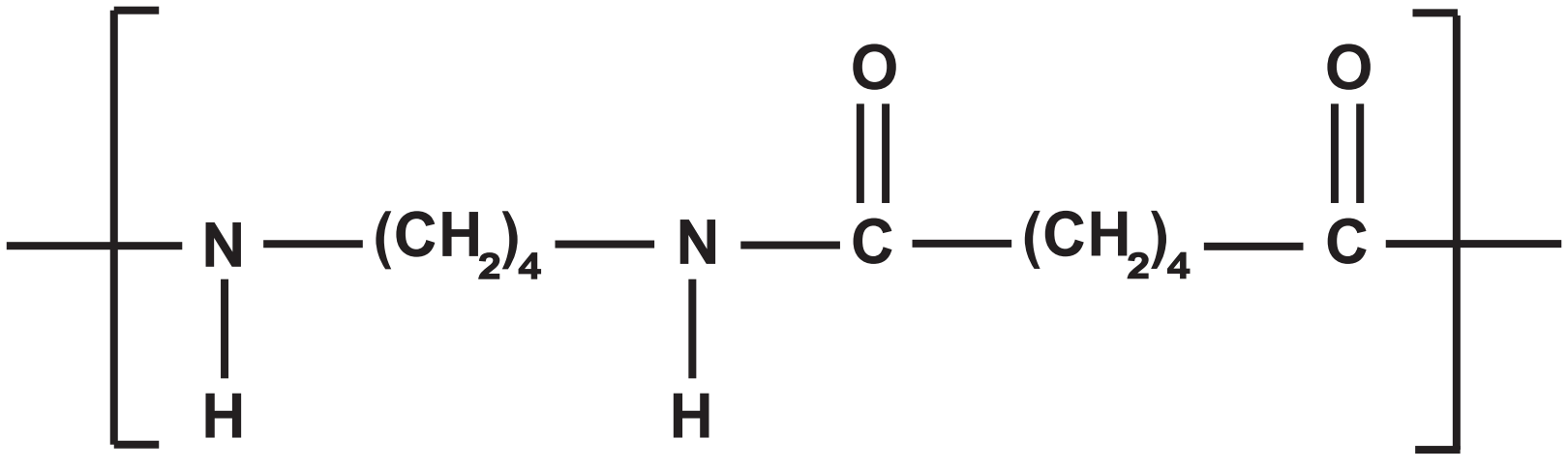
Question 11 (a) (i)



Question 11 (a) (ii)



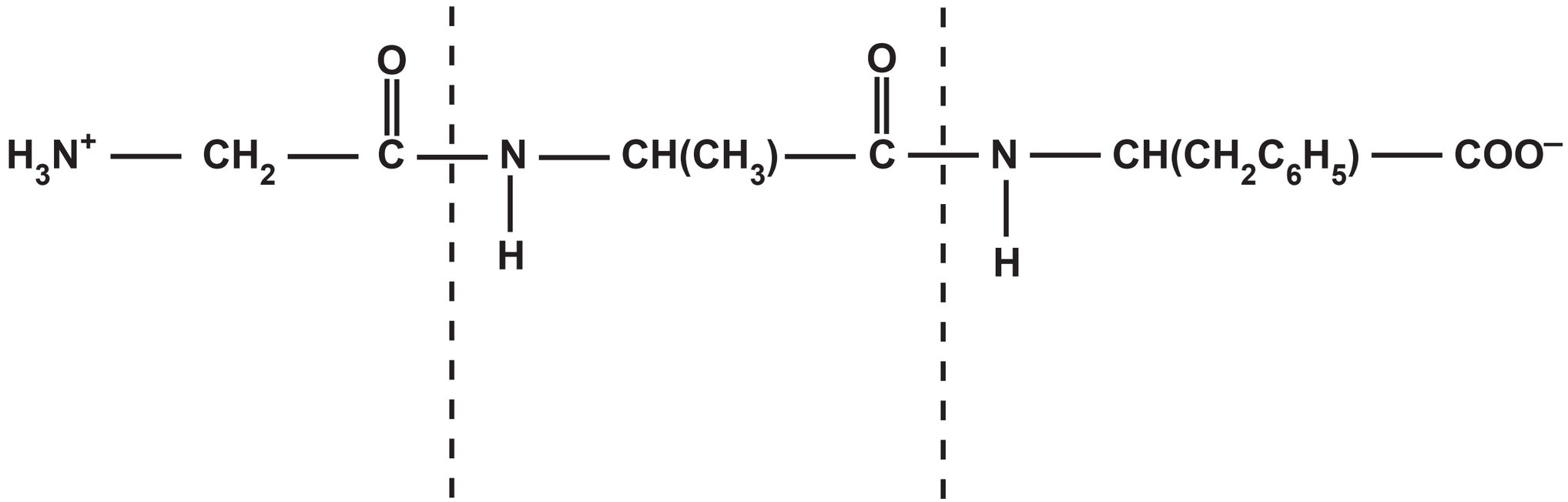
Question 11 (a) (iii)



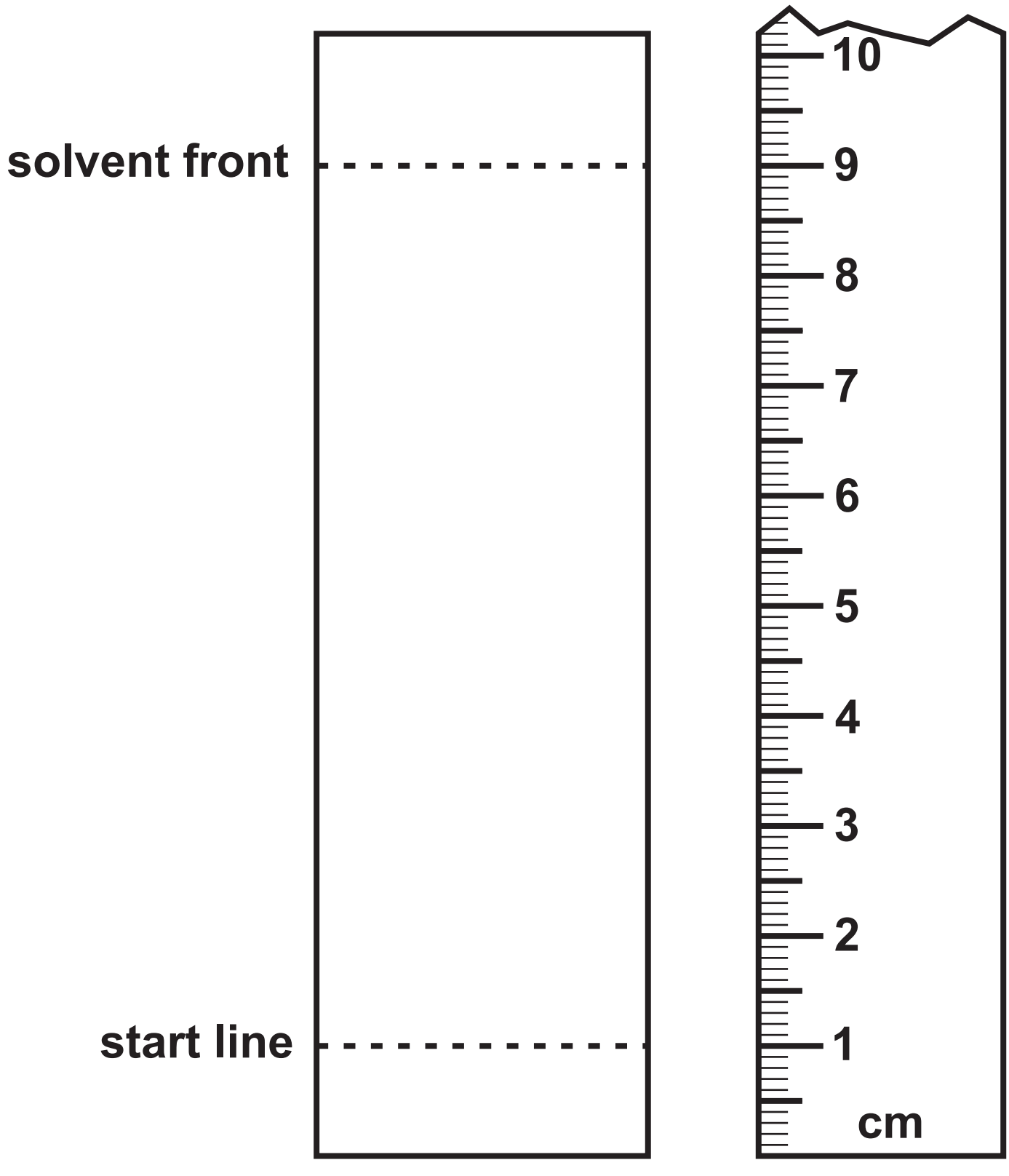
Question 11 (a) (iv)

Question 11 (b)

glycine alanine phenylalanine



Question 11 (b) (iii)



Question 11 (c)