

Question 1: N/A

Question 2: N/A

Question 3: N/A

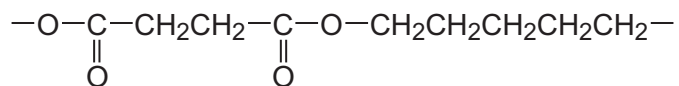
4 Acyl chlorides and acid anhydrides are important compounds in organic synthesis.

4 (a) Outline a mechanism for the reaction of $\text{CH}_3\text{CH}_2\text{COCl}$ with CH_3OH and name the organic product formed.

Mechanism

Name of organic product
(5 marks)

4 (b) A polyester was produced by reacting a diol with a diacyl chloride. The repeating unit of the polymer is shown below.



4 (b) (i) Name the diol used.

.....
(1 mark)

4 (b) (ii) Draw the displayed formula of the diacyl chloride used.

(1 mark)

- 4 (b) (iii) A shirt was made from this polyester. A student wearing the shirt accidentally splashed aqueous sodium hydroxide on a sleeve. Holes later appeared in the sleeve where the sodium hydroxide had been.

Name the type of reaction that occurred between the polyester and the aqueous sodium hydroxide. Explain why the aqueous sodium hydroxide reacted with the polyester.

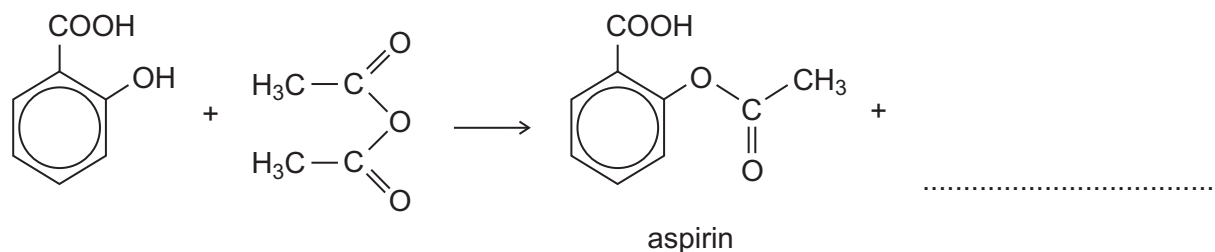
Type of reaction

Explanation

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(3 marks)

- 4 (c) (i) Complete the following equation for the preparation of aspirin using ethanoic anhydride by writing the structural formula of the missing product.



(1 mark)

- 4 (c) (ii) Suggest a name for the mechanism for the reaction in part (c) (i).

.....
(1 mark)

- 4 (c) (iii) Give **two** industrial advantages, other than cost, of using ethanoic anhydride rather than ethanoyl chloride in the production of aspirin.

Advantage 1

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Advantage 2

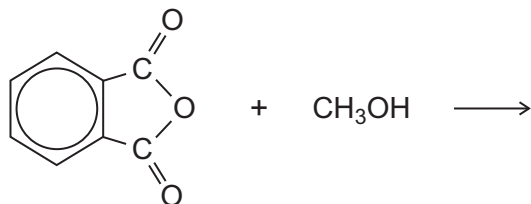
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(2 marks)

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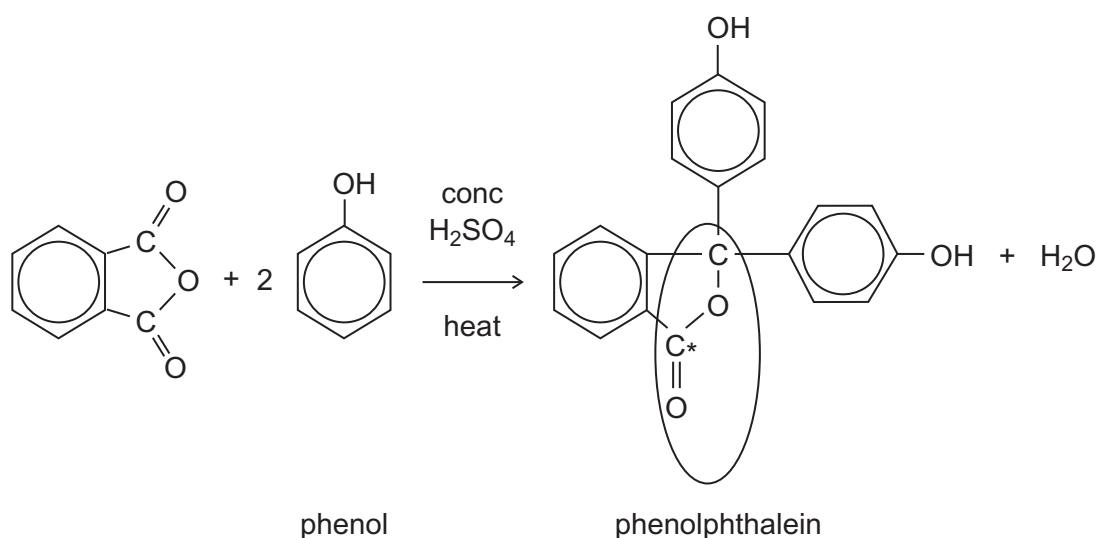
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- 4 (d) Complete the following equation for the reaction of one molecule of benzene-1,2-dicarboxylic anhydride (phthalic anhydride) with one molecule of methanol by drawing the structural formula of the single product.



(1 mark)

- 4 (e) The indicator phenolphthalein is synthesised by reacting phthalic anhydride with phenol as shown in the following equation.



- 4 (e) (i) Name the functional group ringed in the structure of phenolphthalein.

..... (1 mark)

- 4 (e) (ii) Deduce the number of peaks in the ^{13}C n.m.r. spectrum of phenolphthalein.

..... (1 mark)

- 4 (e) (iii) One of the carbon atoms in the structure of phenolphthalein shown above is labelled with an asterisk (*).

Use **Table 3** on the Data Sheet to suggest a range of δ values for the peak due to this carbon atom in the ^{13}C n.m.r. spectrum of phenolphthalein.

..... (1 mark)

- 4 (f) Phenolphthalein can be used as an indicator in some acid–alkali titrations. The pH range for phenolphthalein is 8.3 – 10.0

- 4 (f) (i) For **each** acid–alkali combination in the table below, put a tick (✓) in the box if phenolphthalein could be used as an indicator.

Acid	Alkali	Tick box (✓)
sulfuric acid	sodium hydroxide	
hydrochloric acid	ammonia	
ethanoic acid	potassium hydroxide	
nitric acid	methylamine	

(2 marks)

- 4 (f) (ii) In a titration, nitric acid is added from a burette to a solution of sodium hydroxide containing a few drops of phenolphthalein indicator. Give the colour **change** at the end-point.

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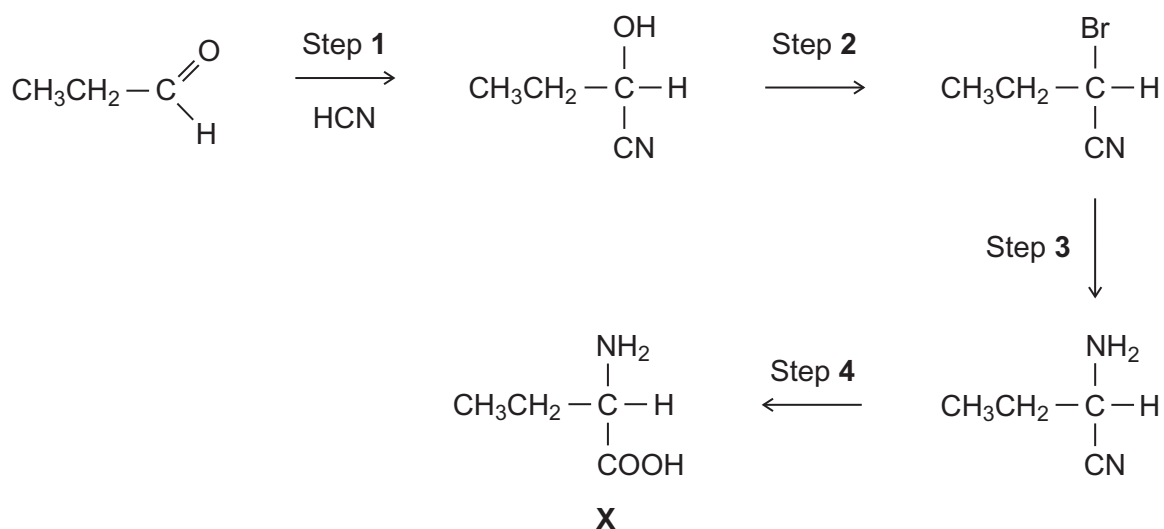
(1 mark)

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- 5 A possible synthesis of the amino acid **X** is shown below.



- 5 (a) Name and outline a mechanism for Step 1.

Name of mechanism

Mechanism

(5 marks)

- 5 (b) Give the IUPAC name of the product of Step 2.

.....

(1 mark)

- 5 (c)** For Step 3, give the reagent, give a necessary condition and name the mechanism.

Reagent

Condition

Name of mechanism

(3 marks)

- 5 (d)** At room temperature, the amino acid **X** exists as a solid.

- 5 (d) (i)** Draw the structure of the species present in the solid amino acid.

(1 mark)

- 5 (d) (ii)** With reference to your answer to part **(d) (i)**, explain why the melting point of the amino acid **X** is higher than the melting point of $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COOH}$

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(2 marks)

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5 (e) There are many structural isomers of **X**, $\text{CH}_3\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$

5 (e) (i) Draw a structural isomer of **X** that is an ethyl ester.

(1 mark)

5 (e) (ii) Draw a structural isomer of **X** that is an amide and also a tertiary alcohol.

(1 mark)

5 (e) (iii) Draw a structural isomer of **X** that has an unbranched carbon chain and can be polymerised to form a polyamide.

(1 mark)

5 (f) Draw the structure of the tertiary amine formed when **X** reacts with bromomethane.

(1 mark)

Section B

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

6 Benzene reacts with ethanoyl chloride in a substitution reaction to form $\text{C}_6\text{H}_5\text{COCH}_3$. This reaction is catalysed by aluminium chloride.

6 (a) Write equations to show the role of aluminium chloride as a catalyst in this reaction. Outline a mechanism for the reaction of benzene. Name the product, $\text{C}_6\text{H}_5\text{COCH}_3$

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(6 marks)

- 6 (b)** The product of the substitution reaction ($\text{C}_6\text{H}_5\text{COCH}_3$) was analysed by mass spectrometry. The most abundant fragment ion gave a peak in the mass spectrum with $m/z = 105$.
Draw the structure of this fragment ion.

(1 mark)

- 6 (c)** When methylbenzene reacts with ethanoyl chloride and aluminium chloride, a similar substitution reaction occurs but the reaction is faster than the reaction of benzene. Suggest why the reaction of methylbenzene is faster.

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(2 marks)

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7 (b)

A fifth bottle was discovered labelled propan-2-ol. The chemist showed, using infrared spectroscopy, that the propan-2-ol was contaminated with propanone.

The chemist separated the two compounds using column chromatography. The column contained silica gel, a polar stationary phase.

The contaminated propan-2-ol was dissolved in hexane and poured into the column. Pure hexane was added slowly to the top of the column. Samples of the eluent (the solution leaving the bottom of the column) were collected.

- Suggest the chemical process that would cause a sample of propan-2-ol to become contaminated with propanone.
- State how the infrared spectrum showed the presence of propanone.
- Suggest why propanone was present in samples of the eluent collected first (those with shorter retention times), whereas samples containing propan-2-ol were collected later.

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(4 marks)

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Turn over for the next question

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Turn over ►

- 8** When the molecular formula of a compound is known, spectroscopic and other analytical techniques can be used to distinguish between possible structural isomers.

Draw **one** possible structure for each of the compounds described in parts **(a)** to **(d)**.

- 8 (a)** Compounds **F** and **G** have the molecular formula $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ and both are dinitrobenzenes.

F has two peaks in its ^{13}C n.m.r. spectrum.

G has three peaks in its ^{13}C n.m.r. spectrum.

F

G

(Space for working)

(2 marks)

- 8 (b)** Compounds **H** and **J** have the molecular formula C_6H_{12}
Both have only one peak in their 1H n.m.r. spectra.
H reacts with aqueous bromine but **J** does not.

H

J

(Space for working)

(2 marks)

Question 8 continues on the next page

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- 8 (c)** **K** and **L** are cyclic compounds with the molecular formula $C_6H_{10}O$
Both have four peaks in their ^{13}C n.m.r. spectra.
K is a ketone and **L** is an aldehyde.

K

L

(Space for working)

(2 marks)

- 8 (d)** Compounds **M** and **N** have the molecular formula $C_6H_{15}N$
M is a tertiary amine with only two peaks in its 1H n.m.r. spectrum.
N is a secondary amine with only three peaks in its 1H n.m.r. spectrum.

M**N***(Space for working)**(2 marks)*

8

Question 9: N/A

Section B

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

10 The reactions of molecules containing the chlorine atom are often affected by other functional groups in the molecule.

Consider the reaction of $\text{CH}_3\text{CH}_2\text{COCl}$ and of $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ with ammonia.

10 (a) For the reaction of $\text{CH}_3\text{CH}_2\text{COCl}$ with ammonia, name and outline the mechanism and name the organic product.

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(6 marks)

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- 10 (c)** Suggest **one** reason why chlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$) does **not** react with ammonia under normal conditions.

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(Extra space) (1 mark)

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