

8 (a) In the electrophilic substitution of arenes, different substituents can direct to different ring positions.

(i) Describe the directing effect of the -NO_2 group. Explain your answer.

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

(ii) The nitration of arenes uses a mixture of concentrated HNO_3 and concentrated H_2SO_4 to generate the NO_2^+ electrophile.

Write an equation for the formation of the NO_2^+ electrophile.

..... [1]

(b) Carbon-carbon bond formation is an important reaction in organic synthesis.

Fig. 8.1 shows the synthesis of compound **Q** from benzene in two reaction steps.

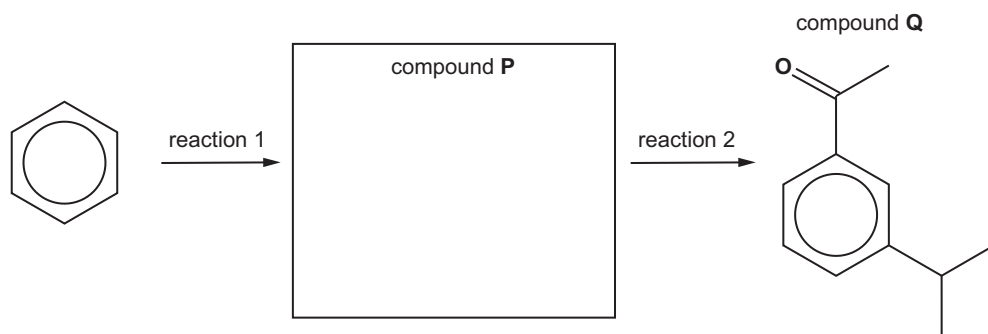


Fig. 8.1

(i) Draw the structure of compound **P** in the box in Fig. 8.1.

[1]

(ii) Suggest reagents and conditions for reactions 1 and 2 in Fig. 8.1.

reaction 1

reaction 2

[2]

(c) Separate samples of $\text{C}_6\text{H}_5\text{Br}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ are added to warm $\text{AgNO}_3(\text{aq})$.

State the expected observations, if any. Explain your answer.

$\text{C}_6\text{H}_5\text{Br}$ with $\text{AgNO}_3(\text{aq})$

$\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ with $\text{AgNO}_3(\text{aq})$

explanation

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.....

.....

[3]

(d) Acyl bromides, RCOBr , react readily with H_2O .

The mechanism of this reaction is similar to that of the reaction of H_2O with acyl chlorides, RCOCl .

(i) Name the mechanism of this reaction.

..... [1]

(ii) Complete the mechanism in Fig. 8.2 for the reaction of RCOBr with H_2O .

Include all relevant lone pairs of electrons, curly arrows, charges and dipoles.

Draw the structure of the intermediate.

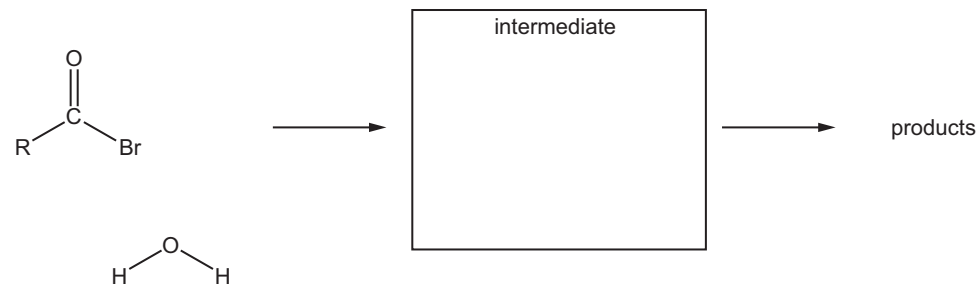


Fig. 8.2

[4]

[Total: 13]

- 8 (a) Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water.

Explain your answer.

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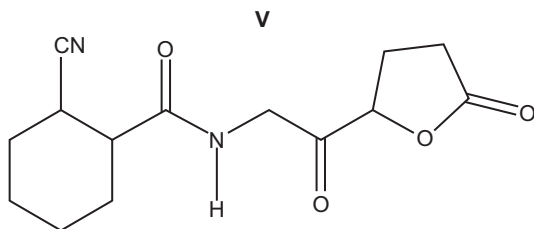
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..... [2]

- (b) The structure of compound **V** is shown.



- (i) Name all the functional groups in **V**.

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..... [2]

- (ii) Deduce the number of possible optical isomers for **V**.

..... [1]

- (iii) Suggest **one** reason, other than better biological activity and lower dosage required, why it is beneficial to synthesise a single optical isomer of **V** for use as a drug.

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..... [1]

- (c) A sample of **V** is hydrolysed with an excess of hot aqueous alkali.

The products are isolated from the reaction mixture at pH 12.

Draw the structures of the **two** organic products of the **complete** alkaline hydrolysis of **V** in Fig. 8.1.

Fig. 8.1

[3]

- (d) A polypeptide formed from four amino acids, **A**, **B**, **C** and **D**, is completely hydrolysed and then analysed by gas–liquid chromatography.

The chromatogram produced is shown in Fig. 8.2.

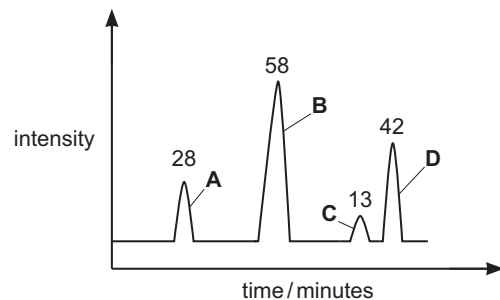


Fig. 8.2

The number above each peak represents the area under the peak.

The area under each peak is proportional to the mass of the respective amino acid in the mixture.

- (i) Calculate the percentage by mass of amino acid **A** in the original mixture.

percentage by mass of amino acid **A** = [1]

- (ii) The retention time for amino acid **D** is the longest.

Explain why **D** has a longer retention time than the **other** amino acids **A**, **B** and **C**.

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

[Total: 11]

Important values, constants and standards

molar gas constant	$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$
Faraday constant	$F = 9.65 \times 10^4 \text{ C mol}^{-1}$
Avogadro constant	$L = 6.02 \times 10^{23} \text{ mol}^{-1}$
electronic charge	$e = -1.60 \times 10^{-19} \text{ C}$
molar volume of gas	$V_m = 22.4 \text{ dm}^3 \text{ mol}^{-1}$ at s.t.p. (101 kPa and 273 K) $V_m = 24.0 \text{ dm}^3 \text{ mol}^{-1}$ at room conditions
ionic product of water	$K_w = 1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ (at 298 K (25 °C))
specific heat capacity of water	$c = 4.18 \text{ kJ kg}^{-1} \text{ K}^{-1}$ (4.18 J g ⁻¹ K ⁻¹)

