

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

(i) Describe the directing effect of the $-\text{NO}_2$ 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.

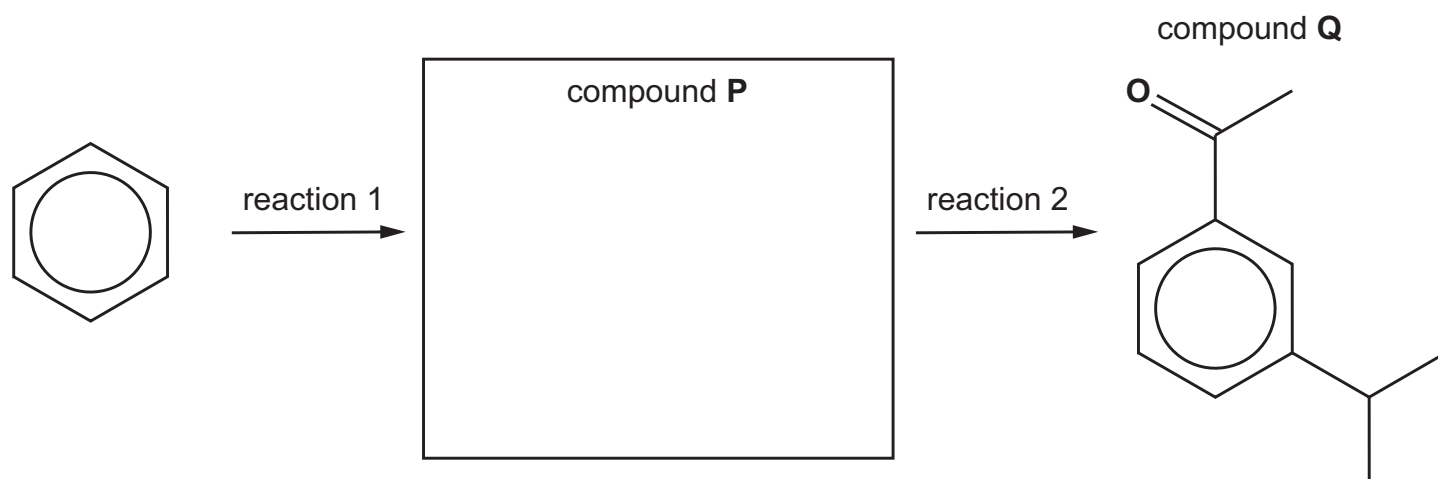


Fig. 8.1

(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

.....

.....

.....

[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.

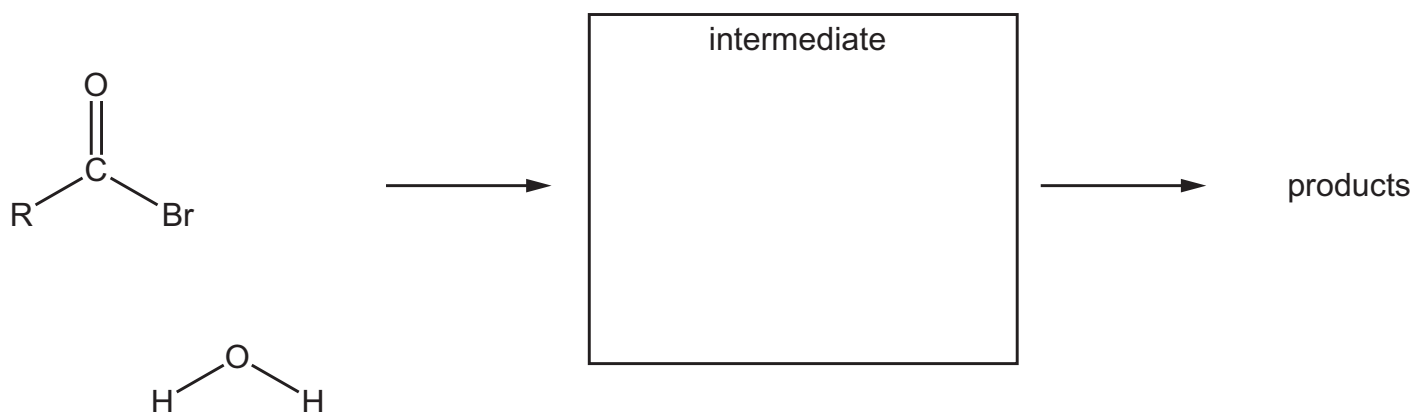


Fig. 8.2

[4]

[Total: 13]

- 8 Asparagine and aspartic acid are two naturally occurring amino acids. Their structures and isoelectric points are shown in Table 8.1.

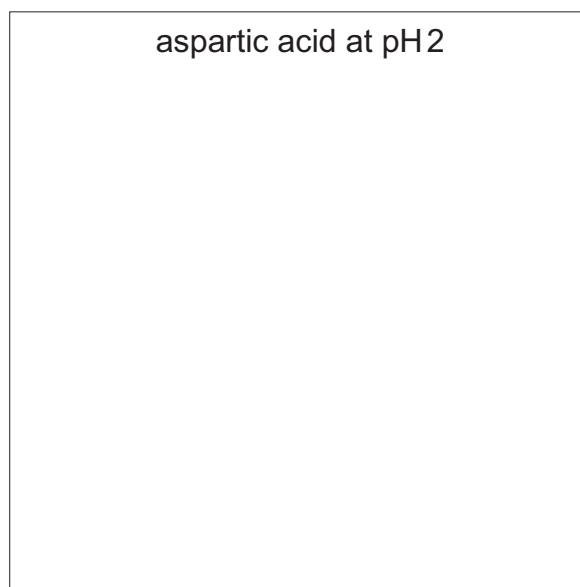
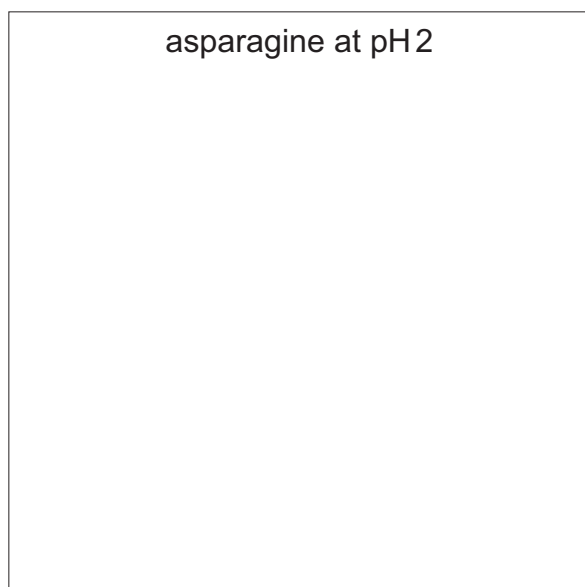
Table 8.1

amino acid	structure	isoelectric point
asparagine	$\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{CONH}_2$	5.41
aspartic acid	$\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{COOH}$	2.77

- (a) Define isoelectric point.

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

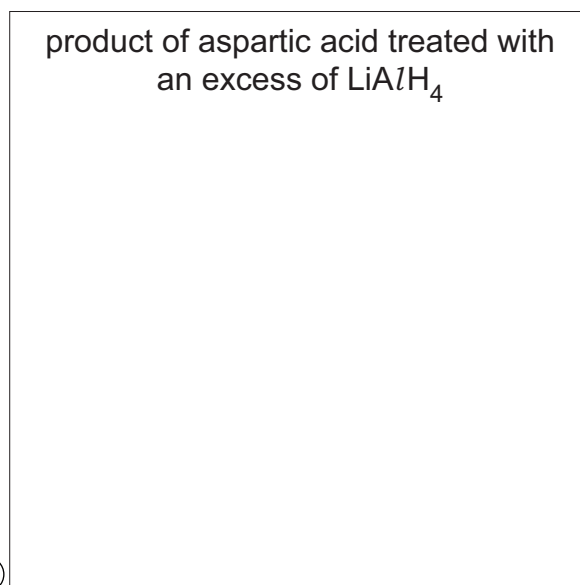
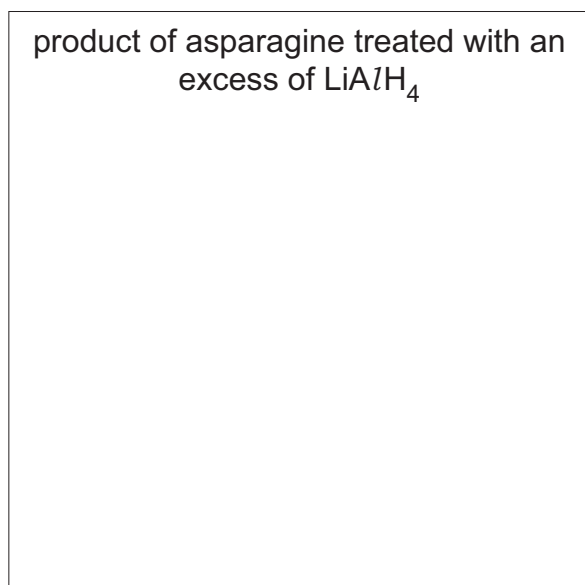
- (b) Draw the structures of asparagine and aspartic acid at pH 2.



[2]

- (c) Asparagine and aspartic acid are treated separately with an excess of LiAlH_4 .

Draw the structures of the organic products of these reactions.



3

- (d) Propanedioic acid, $\text{HOOCCH}_2\text{COOH}$, is treated with an excess of thionyl chloride, SOCl_2 . Propanedioyl chloride, $\text{ClOCCH}_2\text{COC l}$, is formed.

(i) Write an equation for this reaction.

..... [1]

- (ii) Propanedioyl chloride reacts with an excess of asparagine to form compound **G** with molecular formula $\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_8$.

Each molecule of compound **G** has four amide groups.

Draw the structure of compound **G**.

Compound **G**, $\text{C}_{11}\text{H}_{16}\text{N}_4\text{O}_8$

[2]

- (e) Asparagine is hydrolysed with an excess of hot NaOH(aq) .

Draw the structure of the organic product of this reaction.

[2]

- (f) A polymer can form from asparagine, $\text{HOOCCH(NH}_2\text{)CH}_2\text{CONH}_2$, as the only monomer.

Draw a length of the polymer chain containing **three** monomer residues.

Clearly label the repeat unit of the polymer on your diagram.

[3]

(g) Aspartic acid exists in two optically active forms.

- (i)** Plane polarised light is passed through pure samples of these two optically active forms in solutions of the same concentration.

Describe **two** similarities and **one** difference in their effect on the plane polarised light.

similarities

.....

difference

.....

[2]

- (ii)** Give the term used to describe a mixture of equal amounts of the two optically active forms.

..... [1]

[Total: 16]

Question 9 starts on page 20.