Past-paper walk-through

Acyl chlorides ▪ 33.3

eXercise

Questions in this set

- 9701/41 N25 Q8 ▪ 13 marks
- 9701/42 N25 Q8 ▪ 16 marks

Reading the mark scheme

- **B1** a mark that stands on its own – the point is either made or not.
- **M1** a *method* mark: the right approach, even if the number is wrong.
- **A1** an *answer* mark, and it usually needs its M mark first.
- **C1** a working mark on the way to the answer.
- // separates answers the examiner accepts equally.
- **ecf** = error carried forward: a later part is marked on your own earlier answer.
- **owtte** = "or words to that effect" – the wording need not match.

Question 8

9701/41 N25 ▪ Q8 ▪ 13 marks

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.

Question 8

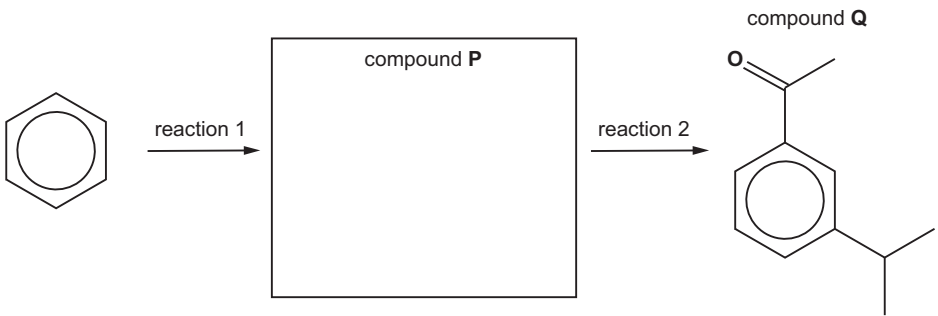
(ii) The nitration of arenes uses a mixture of concentrated HNO_3 and concentrated H_2SO_4 to generate the NO_2^+ electrophile.

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

Question 8

(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.



Question 8

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.

Question 8

Question 8

[2]

(c) Separate samples of C_6H_5Br and $C_6H_5CH_2Br$ are added to warm $AgNO_3(aq)$.

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

Question 8

Question 8

Question 8

[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, RCOC*l*.

(i) Name the mechanism of this reaction.

Question 8

(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.

Question 8

Question 8

Fig. 8.2

[4]

[Total: 13]

Solution 8

(a)(i)

Mark scheme

- NO2 group directs to 3 (and 5) / meta position AND due to being an electron-withdrawing / electronegative group
- 1

Solution 8

(a)(ii)

Mark scheme

- $HNO_3 + H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_2O$
- OR $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$
- 1

Solution 8

(b)(i)

Mark scheme

- 1

(b)(ii)

Mark scheme

- M1: (reaction 1) ethanoyl chloride / CH3COCl AND Al Cl 3
- M2: (reaction 2) 2-bromopropane / (CH3)2CHBr AND FeBr3
- 2

Solution 8

(c) Mark scheme

- M1:
- with C6H5Br
- no change / no precipitate AND
- with C6H5CH2Br
- cream precipitate
- in C6H5Br
- M2: lone pair / p-orbital on Br delocalised / overlaps with ring / π system
- M3: C–Br bond stronger / has partially double bond character

Solution 8

- 3
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Solution 8

(d)(i)

Mark scheme

- (nucleophilic) addition–elimination
- 1

Solution 8

(d)(ii) Mark scheme

- M1 M2:
- ▪
- lone pair on O
- ▪
- curly arrow from (lone pair) O (in H2O) to C (of C=O)
- ▪
- correct dipole on C=O
- ▪

Solution 8

- curly arrow from the C=O bond to O atom
- any two [1], all four [2]
- M3: correct intermediate
- M4: curly arrow from (lone pair on) O(–) to C–O bond AND curly arrow from C–Br to Br
- 4

Question 8

9701/42 N25 ▪ Q8 ▪ 16 marks

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	$HOOCCH(NH_2)CH_2CONH_2$	5.41
aspartic acid	$HOOCCH(NH_2)CH_2COOH$	2.77

(a) Define isoelectric point.

Question 8

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

asparagine at pH 2	aspartic acid at pH 2

Question 8

[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.

product of asparagine treated with an excess of $LiAlH_4$	product of aspartic acid treated with an excess of $LiAlH_4$

Question 8

[2]

(d) Propanedioic acid, $HOOCCH_2COOH$, is treated with an excess of thionyl chloride, $SOCl_2$. Propanedioyl chloride, $ClOCCH_2COCl$, is formed.

(i) Write an equation for this reaction.

Question 8

(ii) Propanedioyl chloride reacts with an excess of asparagine to form compound **G** with molecular formula $C_{11}H_{16}N_4O_8$.

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

Draw the structure of compound **G**.

Compound **G**, $C_{11}H_{16}N_4O_8$

Question 8

[2]

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

Draw the structure of the organic product of this reaction.

Question 8

[2]

(f) A polymer can form from asparagine, $HOOCCH(NH_2)CH_2CONH_2$, 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.

Question 8

[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.

Question 8

Question 8

Question 8

Question 8

[2]

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

Question 8

[Total: 16]

Question 8

Question 9 starts on page 20.

Solution 8

(a)

Mark scheme

- the pH at which an amino acid exists as a zwitterion
- 1

Solution 8

(b)

Mark scheme

- M1: [HOOCCH(NH3)CH2CONH2]+
- M2: [HOOCCH(NH3)CH2COOH]+
- 2
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Solution 8

(c)

Mark scheme

- M1: HOCH2CH(NH2)CH2CH2NH2
- M2: HOCH2CH(NH2)CH2CH2OH
- 2

Solution 8

(d)(i)

Mark scheme

- HOOCCH2COOH + 2SOCl2 → ClOCCH2COCl + 2SO2 + 2HCl

1

- 1

Solution 8

(d)(ii)

Mark scheme

- HOOCCH(CH2CONH2)NHCOCH2CONHCH(CH2CONH2)COOH
- M1: three molecules joined, with four correct amide groups only
- M2: whole structure correct as above, displayed formula accepted, skeletal formula as below accepted
- 2

Solution 8

(e)

Mark scheme

- M1: hydrolysis of amide to carboxylate ion
- M2: hydrolysis of –COOH to carboxylate ion and rest of molecule
- –OOCCH(NH2)CH2COO–
- 2
- 9701/42
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Solution 8

(f) Mark scheme

- ▪
- three monomer residues
- ▪
- all linkages correct
- ▪
- correct trailing bonds
- ▪
- repeat unit marked contains correct atoms

Solution 8

- Any two [1], any three [2], all four [3]
- CH2CONH2 CH2CONH2
- | |
- –COCHNH–[–COCHNH–]–COCHNH–
- |
- CH2CONH2
- 3

Solution 8

(g)(i) Mark scheme

- ▪
- rotate the plane of the plane polarised light
- ▪
- by the same angle
- ▪
- in opposite directions
- Any two [1], all three [2]
- 2

Solution 8

(g)(ii)

Mark scheme

- racemic mixture
- 1