Week 49

A-Level Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

Contents 目录

33. Carboxylic acids and derivatives

Starter Quiz · 课前小测

A-Level Chemistry Name: _____ Score: _____

1. Oxidising methylbenzene with hot alkaline $KMnO_4$ gives:
   - ☐ benzoic acid (the side-chain becomes –COOH)
   - ☐ nitrobenzene
   - ☐ cyclohexane
   - ☐ phenol
2. An ester can be made at room temperature by reacting an acyl chloride with:
   - ☐ an alcohol or a phenol
   - ☐ an alkane
   - ☐ water only
   - ☐ an amine
3. An acyl chloride reacting with ammonia gives:
   - ☐ an amide (plus HCl)
   - ☐ an ester
   - ☐ a carboxylic acid
   - ☐ an alkene
4. Which carboxylic acid can be oxidised further?
   - ☐ methanoic acid (HCOOH)
   - ☐ ethanoic acid
   - ☐ propanoic acid
   - ☐ benzoic acid
5. Reacting phenol with benzoyl chloride gives:
   - ☐ phenyl benzoate
   - ☐ ethyl ethanoate
   - ☐ benzoic acid
   - ☐ phenol again
6. Making an ester from an acyl chloride happens at room temperature.

   ☐ True ☐ False

7. An ester is hydrolysed by hot aqueous alkali in a reaction called _____.

   _____

8. Carboxylic acids react with carbonates to release carbon dioxide.

   ☐ True ☐ False

9. Esters often have sweet, fruity smells.

   ☐ True ☐ False

10. Acyl chlorides react vigorously with water to give a carboxylic acid and _____ chloride gas.

    _____

A-Level Chemistry

1. **benzoic acid (the side-chain becomes –COOH)**

   The whole side-chain is oxidised to a –COOH group, giving benzoic acid.

2. **an alcohol or a phenol**

   Both alcohols and phenols react with acyl chlorides to give esters (+ HCl).

3. **an amide (plus HCl)**

   Ammonia (or a 1°/2° amine) reacts with an acyl chloride to give an amide.

4. **methanoic acid (HCOOH)**

   Methanoic and ethanedioic acids can be oxidised further (e.g. to CO_2); most carboxylic acids cannot.

5. **phenyl benzoate**

   A phenol + an acyl (benzoyl) chloride forms the ester phenyl benzoate.

6. **True**

   Acyl chlorides are very reactive, so the reaction proceeds quickly at room temperature.

7. **saponification**

   It gives a carboxylate salt and an alcohol.

8. **True**

   A test for the acid group.

9. **True**

   They are used as flavourings and perfumes.

10. **hydrogen**

    Misty fumes of HCl form.

A-LEVEL CHEMISTRY • EXERCISE SHEET

33.1 Carboxylic acids

Name: _____ Class: _____ Date: _____ **Total: 32 marks**

KEY WORDS acidity 酸性 • acyl chloride 酰氯 • phenol 苯酚 • carboxylic acid 羧酸 • alcohol 醇

Objective

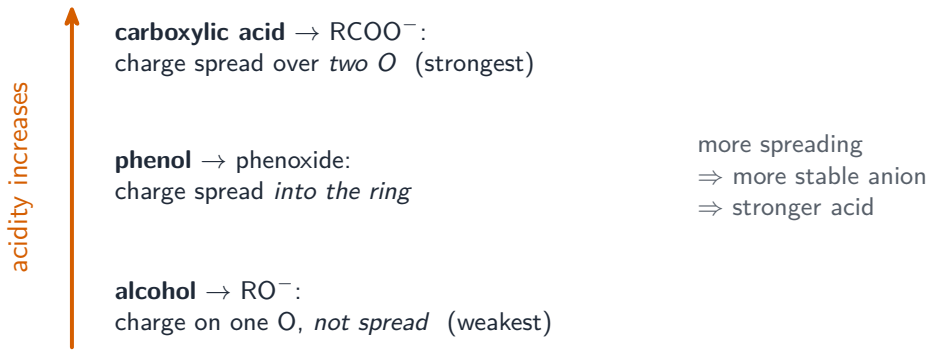
Build the skills to answer exam questions on **carboxylic acids** 羧酸 — making them, the special acids that oxidise further, and the trends in **acidity** 酸性.

You must be able to:

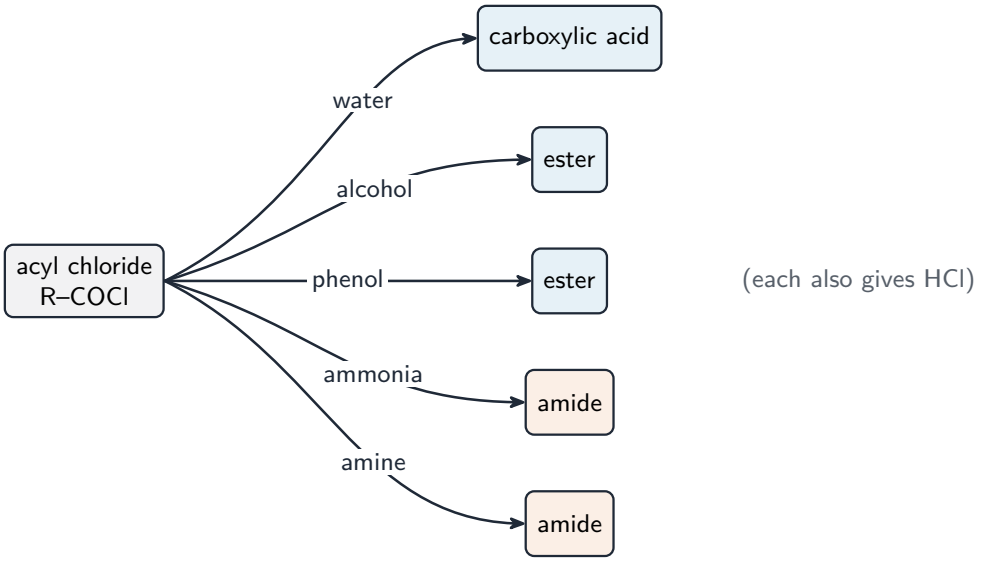
- make benzoic acid by side-chain oxidation; make an acyl chloride from an acid
- recall which carboxylic acids can be oxidised further
- explain the acidity order alcohol < phenol < carboxylic acid
- explain how chlorine substituents affect acid strength

1 Worked examples

■ Acidity trends



The more the negative charge on the conjugate base is spread out, the more stable the ion and the stronger the acid



Carboxylic acids and their acyl chloride reactions

- **acidity:** alcohol < phenol < **carboxylic acid** — the carboxylate spreads its charge over **two** oxygens.
- **electron-withdrawing** Cl atoms (inductive effect) pull electron density away, spread the charge more → **stronger** acid; more Cl (and closer to –COOH) = stronger.
- **make benzoic acid:** methylbenzene + hot alkaline $KMnO_4$, then acid (whole side-chain → –COOH).

Making them, testing them, and the acidity comparison

Four routes to a carboxylic acid:

From	Reagents
a primary alcohol	$K_2Cr_2O_7$ / dilute H_2SO_4, heated **under reflux** (distilling instead stops at the aldehyde)
an aldehyde	the same oxidising mixture
a nitrile	hydrolysis with dilute acid, heated
an ester or amide	hydrolysis, acid or alkaline (alkaline gives the salt, then acidify)

Two acids oxidise further, and that is examinable. Methanoic acid, HCOOH, still has an H on the carbonyl carbon, so it behaves as an aldehyde too: it reduces Fehling's and Tollens'. **Ethanedioic acid**, $(COOH)_2$, is oxidised by warm acidified $KMnO_4$ to carbon dioxide, decolourising the purple solution.

The reactions to know: with a reactive metal → salt + hydrogen; with a carbonate → salt + water + **carbon dioxide** (effervescence, the test that distinguishes an acid from a phenol); with an alcohol and an acid catalyst → an ester; with $LiAlH_4$ → a primary alcohol; with PCl_5 or $SOCl_2$ → an acyl chloride.

Why a carboxylic acid is more acidic than an alcohol or phenol — the standard 3-mark comparison:

- In the **carboxylate** ion the negative charge is delocalised over **two oxygen atoms** and both C–O bonds are equal, so the anion is very stable and the equilibrium lies well to the right.
- In the **phenoxide** ion the charge is delocalised into the **ring**, which stabilises it but less effectively, so phenol is a weaker acid.
- In an **alkoxide** the charge is localised on **one oxygen**, with an electron-releasing alkyl group making it worse; ethanol is barely acidic at all.

Order: carboxylic acid > phenol > water > alcohol. **Electron-withdrawing groups increase acidity** by pulling charge away from the carboxylate: chloroethanoic acid is stronger than ethanoic acid, and trichloroethanoic acid stronger still.

2 Practice

2.1 Give the reagents to oxidise methylbenzene to benzoic acid. [2]

2.2 State which is the stronger acid: ethanoic acid or chloroethanoic acid. [1]

2.3 Give the reagents and conditions for making propanoic acid from propan-1-ol. [3]

2.4 State the observation when ethanoic acid is added to sodium carbonate, and name the gas. [2]

2.5 Explain why chloroethanoic acid is a stronger acid than ethanoic acid. [2]

3 Exam-style questions

3.1 A carboxylic acid is more acidic than phenol because its conjugate base spreads the negative charge over: [1]

- **A** one oxygen atom
- **B** two oxygen atoms
- **C** the benzene ring only
- **D** no atoms

3.2 Which is the **strongest** acid? [1]

- **A** ethanoic acid, CH_3COOH
- **B** chloroethanoic acid, $CH_2ClCOOH$
- **C** dichloroethanoic acid, $CHCl_2COOH$
- **D** trichloroethanoic acid, CCl_3COOH

3.3 Explain, in terms of the conjugate base, why a carboxylic acid is more acidic than an alcohol. [2]

3.4 Trichloroethanoic acid is a much stronger acid than ethanoic acid. Explain why, in terms of the inductive effect. [3]

3.5 (a) Give the reagents and conditions for oxidising butan-1-ol to butanoic acid, and explain why reflux rather than distillation is used. [3]

(b) Explain, in terms of the anion formed, why ethanoic acid is a stronger acid than ethanol. [3]

(c) Explain why phenol is a weaker acid than ethanoic acid. [2]

(d) Describe a chemical test that would distinguish ethanoic acid from phenol, giving the reagent and the observation with each. [3]

(e) Methanoic acid gives a positive result with Tollens' reagent, but ethanoic acid does not. Explain why. [2]

(f) Name the product and give the reagent when butanoic acid is treated with $LiAlH_4$. [2]

Solutions

2.1 hot alkaline $KMnO_4$ (potassium manganate(VII)); then dilute acid (acidify).

2.2 chloroethanoic acid.

2.3 Acidified potassium dichromate(VI); heat; under reflux.

2.4 Effervescence, or bubbles of gas; carbon dioxide.

2.5 The chlorine atom is electron-withdrawing, so it pulls electron density away from the carboxylate ion and spreads the negative charge further, making the anion more stable and the acid stronger.

3.1 B. The carboxylate ion spreads its negative charge over two oxygen atoms.

3.2 D. Three electron-withdrawing chlorine atoms spread the charge most, giving the strongest acid.

3.3 when a carboxylic acid loses H^+, the charge is delocalised over two oxygen atoms, making a very stable carboxylate ion; an alkoxide (RO^-) cannot spread its charge, so it is less stable and the alcohol is far less acidic.

3.4 chlorine is electron-withdrawing and pulls electron density away through the inductive effect; this helps spread out the negative charge on the conjugate base, stabilising the ion; three Cl atoms in CCl_3COOH do this much more than the CH_3 in ethanoic acid, so it is a far stronger acid.

3.5 (a) Acidified potassium dichromate(VI), heated; reflux returns the vapour to the flask so the oxidation continues to the acid, while distillation would remove the aldehyde as soon as it formed.
(b) In the ethanoate ion the negative charge is delocalised over two oxygen atoms, so the anion is much more stable; in the ethoxide ion the charge is localised on one oxygen and the alkyl group releases electron density towards it, making it less stable, so the equilibrium lies much further left.
(c) In the phenoxide ion the charge is delocalised into the benzene ring rather than over two oxygens, which stabilises it less effectively than in a carboxylate.
(d) Add aqueous sodium carbonate to each; ethanoic acid gives effervescence of carbon dioxide; phenol gives no reaction, because it is too weak an acid to release carbon dioxide from a carbonate.
(e) Methanoic acid has a hydrogen atom attached to the carbonyl carbon, so it has an aldehyde group and can be oxidised further, reducing the Tollens' reagent.
(f) Butan-1-ol; lithium tetrahydridoaluminate in dry ether.

7 **(a)** State the relative acidities of bromoethanoic acid, $BrCH_2COOH$, chloroethanoic acid, $C\ell CH_2COOH$, ethanoic acid, CH_3COOH and ethanol, CH_3CH_2OH.

Explain your answer.

....
most acidic least acidic

.....

.....

.....

.....

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.....

.....

[4]

(b) Fig. 7.1 shows the reaction of methylbenzene and ethanedioic acid with $KMnO_4$.

Predict the major carbon-containing product for each of these reactions.

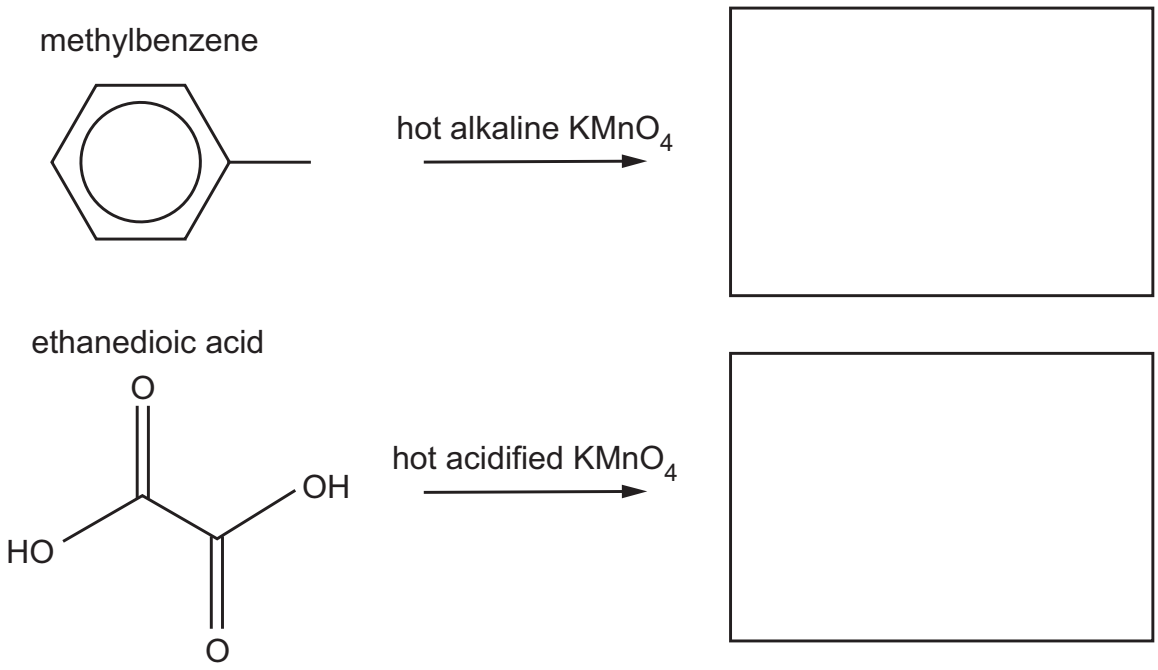
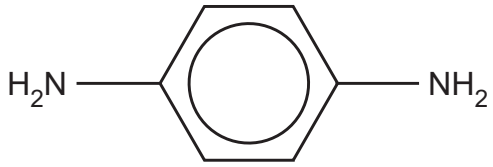


Fig. 7.1

[2]

(c) Polyamide **X** can be synthesised from ethanedioic acid and benzene-1,4-diamine.

benzene-1,4-diamine



(i) Draw the repeat unit of polyamide **X** in the box.

The new functional group formed should be shown displayed.

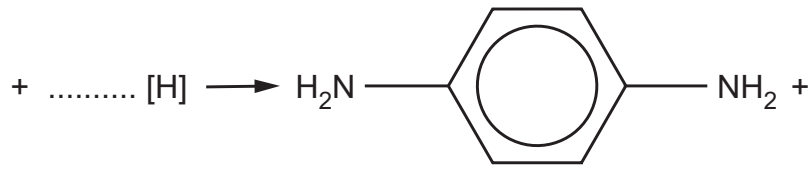
polyamide **X**

[2]

(ii) Benzene-1,4-diamine can be formed by reduction of 1,4-dinitrobenzene.

Complete the equation for this reduction.

[H] represents one atom of hydrogen from a reducing agent.



.....

[1]

(d) Fig. 7.2 shows the two-step synthesis of the azo compound **W**.

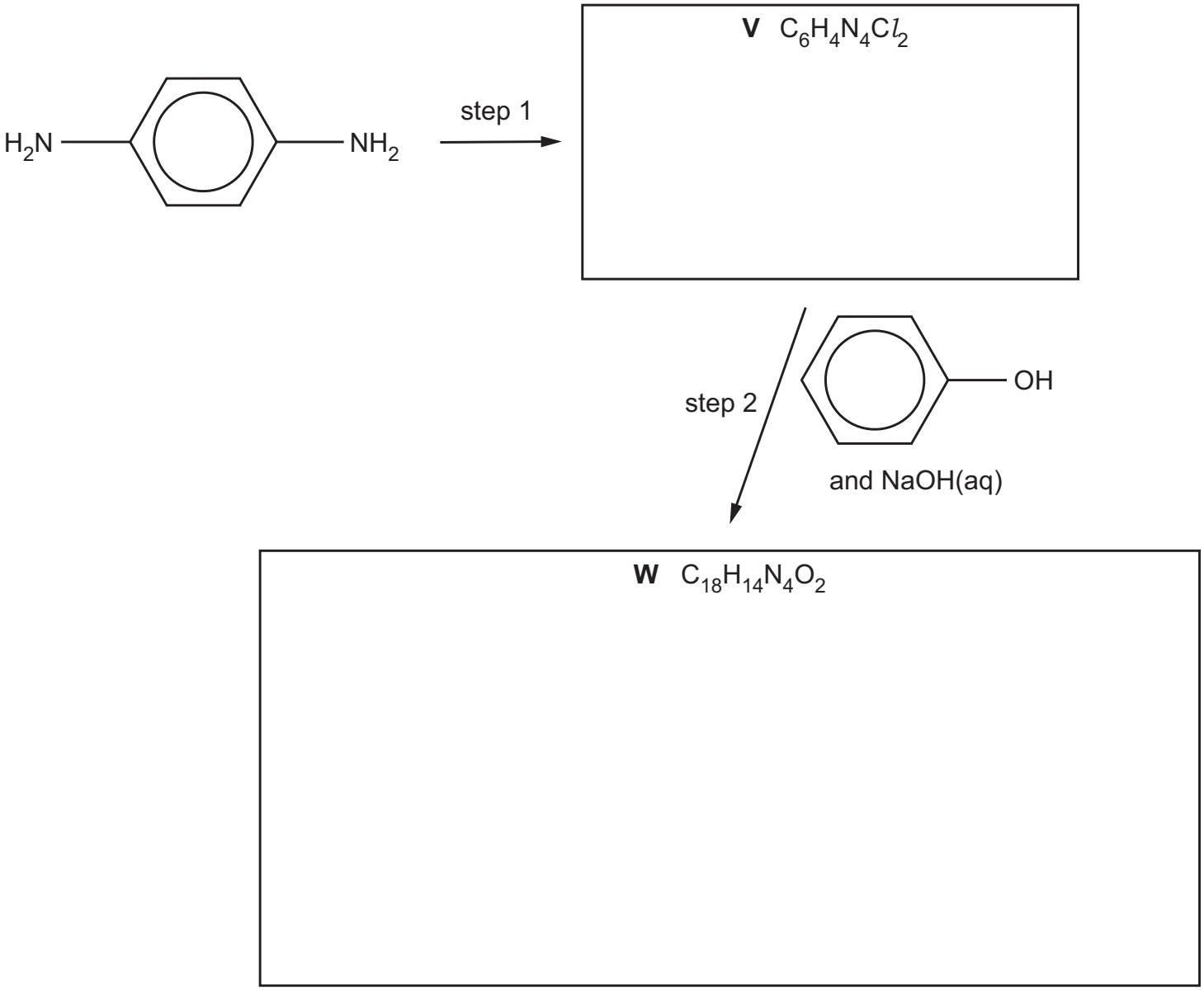


Fig. 7.2

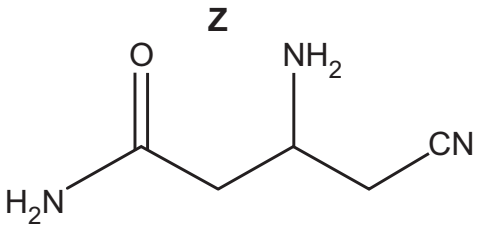
(i) Suggest structures for compounds **V** and **W** and draw them in the boxes in Fig. 7.2. [2]

(ii) Give the reagents and conditions for step 1.

..... [1]

[Total: 12]

6 **(a)** Compound **Z** is used in organic synthesis.



Complete Table 6.1 to show the number of sp, sp^2 and sp^3 hybridised carbon atoms present in one molecule of **Z**.

Table 6.1

type of hybridisation	sp	sp^2	sp^3
number of carbon atoms			

[1]

(b) **Z** can undergo different reactions, as shown in Fig. 6.1.

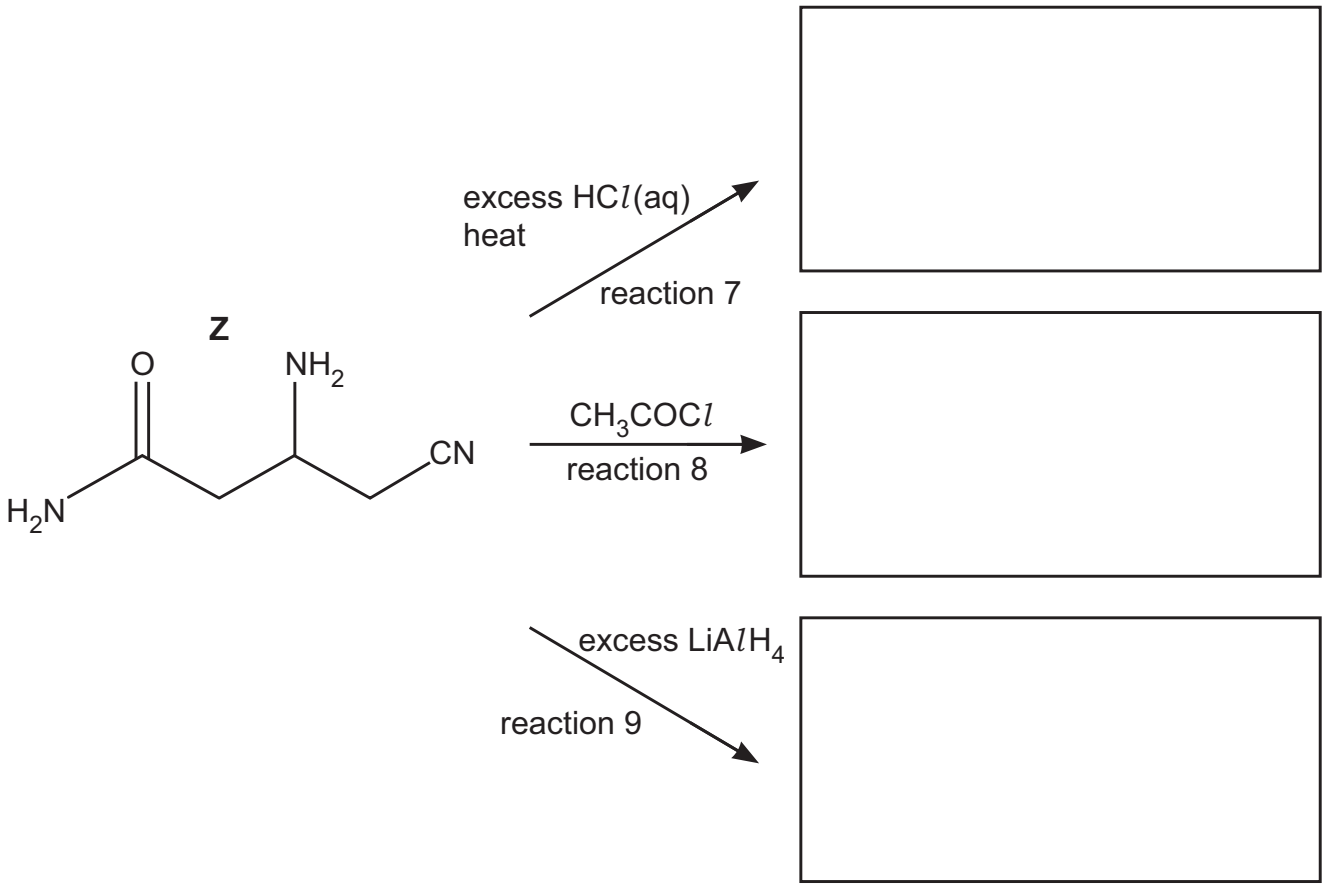


Fig. 6.1

(i) Name the **two** types of reaction occurring in reaction 7 in Fig. 6.1.

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

(ii) Draw the structures of the organic products of reactions 7, 8 and 9 in Fig. 6.1. [4]

(c) Compound **Z** is dissolved in D_2O and analysed by carbon-13 NMR and proton (^1H) NMR spectroscopy.

(i) Predict the number of peaks in the carbon-13 NMR spectrum of **Z**.

..... [1]

(ii) The proton (^1H) NMR spectrum of **Z** in D_2O gives three peaks for the proton environments, labelled **a**, **b** and **c**, as shown on Fig. 6.2.

Z

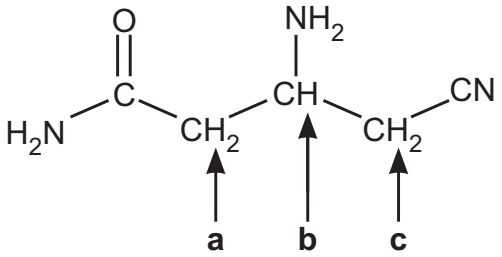


Fig. 6.2

Complete Table 6.2 for the proton (^1H) NMR spectrum of **Z** in D_2O.

Table 6.2

proton environment	**a**	**b**	**c**
name of splitting pattern			
chemical shift range, δ/ppm			

[2]

Table 6.3

environment of proton	example	chemical shift range, δ/ppm
alkane	–C**H**$_3$, –C**H**$_2$–, >C**H**–	0.9–1.7
alkyl next to C=O	C**H**$_3$–C=O, –C**H**$_2$–C=O, >C**H**–C=O	2.2–3.0
alkyl next to nitrile	–C**H**$_2$–CN	2.0–3.0
alkyl next to electronegative atom	C**H**$_3$–O, –C**H**$_2$–O, –C**H**$_2$–N	3.2–4.0
attached to alkene	=C**H**R	4.5–6.0
alkyl amine	R–N**H**–	1.0–5.0
amide	RCON**H**R	5.0–12.0

[Total: 9]

33.2 Esters

Name: _____ Class: _____ Date: _____ **Total: 22 marks**

KEY WORDS acyl chloride 酰氯 • ester 酯 • phenol 苯酚 • benzoic acid 苯甲酸 • alcohol 醇

Objective

Build the skills to answer exam questions on **esters** 酯 — how they are made from an acyl chloride, naming them, and recognising the ester link.

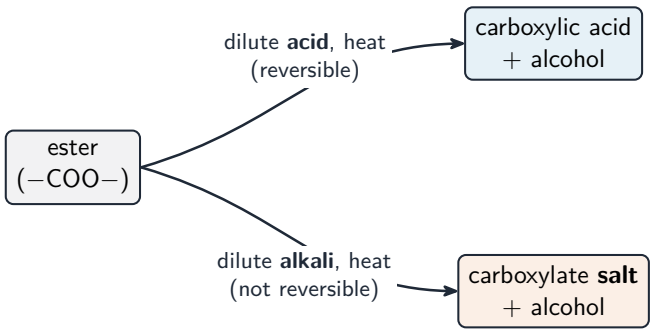
You must be able to:

- make an ester from an alcohol (or phenol) and an acyl chloride
- name an ester from its structure (and vice versa)
- write equations for ester formation

1 Worked examples

■ Making and naming esters

Alcohol (or phenol) + acyl chloride → ester + HCl, at room temperature



Esters are hydrolysed back to acid and alcohol

- **alcohol/phenol + acyl chloride → ester + HCl.**
- e.g. ethanol + ethanoyl chloride → ethyl ethanoate; phenol + benzoyl chloride → phenyl benzoate.

- **naming:** the alcohol part gives the first word ("ethyl"), the acid part gives the second ("…anoate").

2 Practice

2.1 Name the ester $CH_3COOCH_2CH_3$. [1]

2.2 Name the two organic starting materials (an acyl chloride + an alcohol) for ethyl ethanoate. [2]

3 Exam-style questions

3.1 The ester $HCOOCH_3$ is named: [1]

- **A** methyl methanoate
- **B** methyl ethanoate
- **C** ethyl methanoate
- **D** methanoyl methane

3.2 Phenyl benzoate is made from benzoyl chloride and: [1]

- **A** benzene
- **B** phenol
- **C** benzoic acid
- **D** phenylamine

3.3 Methanol reacts with ethanoyl chloride.

(a) Write the equation. [2]

(b) Name the ester formed. [1]

3.4 Draw the structure of propyl methanoate and circle the **ester link**. [2]

3.5 Ethanoyl chloride, CH_3COCl, reacts with propan-1-ol.

(a) Write the equation, name the ester formed, and state one observation. [3]

(b) Explain why an acyl chloride is used rather than the carboxylic acid when a high yield is wanted. [3]

(c) Draw the ester link, and give the systematic name of the ester made from **propanoyl chloride and ethanol**. [3]

(d) The ester in (a) is refluxed with dilute sulfuric acid. Name the two organic products, and explain why an excess of water is used. [3]

Solutions

2.1 ethyl ethanoate.

2.2 ethanoyl chloride; ethanol.

3.1 A. HCOO– is methanoate; $–CH_3$ is methyl → methyl methanoate.

3.2 B. Phenol + benzoyl chloride → phenyl benzoate + HCl.

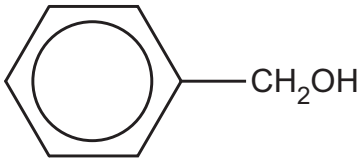
3.3 (a) $CH_3COCl + CH_3OH \rightarrow CH_3COOCH_3 + HCl$.
(b) methyl ethanoate.

3.4 $HCOOCH_2CH_2CH_3$ drawn out; the –COO– ester link circled.

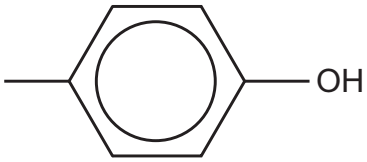
3.5 (a) $CH_3COCl + CH_3CH_2CH_2OH \rightarrow CH_3COOCH_2CH_2CH_3 + HCl$; the ester is **propyl ethanoate**; steamy white fumes of hydrogen chloride are seen.
(b) The acyl chloride reaction goes essentially to **completion** — it is not an equilibrium — because the HCl escapes as a gas and cannot react back; esterification with the acid is reversible and stops at about 65% conversion.
(c) The ester link is $-C(=O)-O-$ drawn with the carbonyl double bond and the single bond to the second oxygen; the ester from propanoyl chloride and ethanol is **ethyl propanoate**.
(d) **Ethanoic acid** and **propan-1-ol**; acid hydrolysis is reversible, so a large excess of water pushes the equilibrium towards the products.

7 Phenylmethanol and 4-methylphenol are isomers.

phenylmethanol



4-methylphenol



(a) Complete Table 7.1 to show the relative acidities of benzoic acid (C_6H_5COOH), phenylmethanol, 4-methylphenol and water.

Explain your answer.

Table 7.1

	name of compound
most acidic ↓	
least acidic	

explanation .....

.....

.....

.....

.....

.....

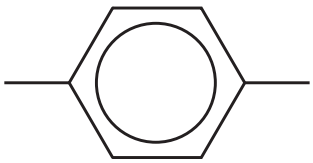
.....

.....

[4]

(b) 4-methylphenol reacts readily with sodium.

Complete the equation for this reaction.



+ ..... ➚

[1]

(c) Under certain conditions, ethane-1,2-diol, $HOCH_2CH_2OH$, reacts with propane-1,3-dioic acid, $HOOCCH_2COOH$, to form different organic products, as shown in Fig. 7.1.

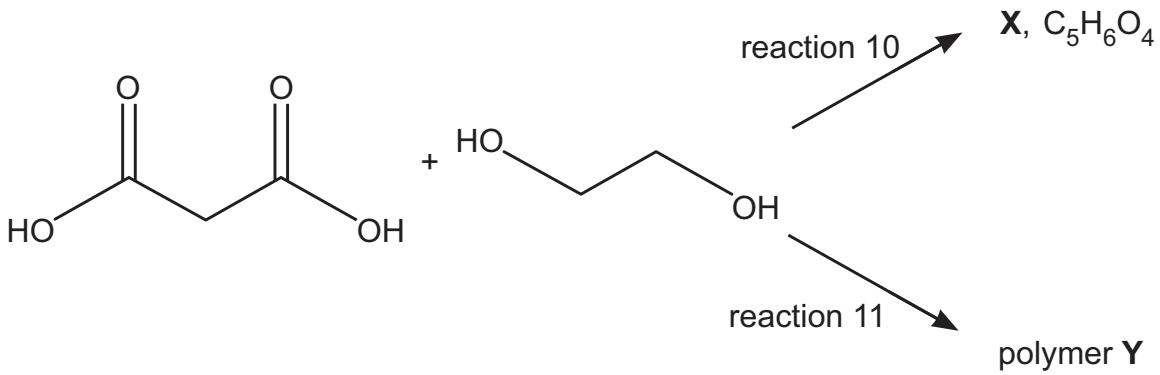


Fig. 7.1

(i) **X** does **not** react with Na metal.

Draw the structure of the organic product **X**, $C_5H_6O_4$, shown in Fig. 7.1.

[1]

(ii) Reactions 10 and 11 in Fig. 7.1 are different types of reaction.

Name the type of reaction for reaction 10 and for reaction 11.

reaction 10 .....

reaction 11 .....

[1]

(iii) Draw a section of polymer **Y** showing only **one** repeat unit.

The new functional group formed should be displayed.

[2]

[Total: 9]

A-LEVEL CHEMISTRY • EXERCISE SHEET

33.3 Acyl chlorides

Name: _____ Class: _____ Date: _____ **Total: 28 marks**

KEY WORDS acyl chloride 酰氯 • addition–elimination 加成消去 • amide 酰胺 • amine 胺 • hydrolysis 水解

Objective

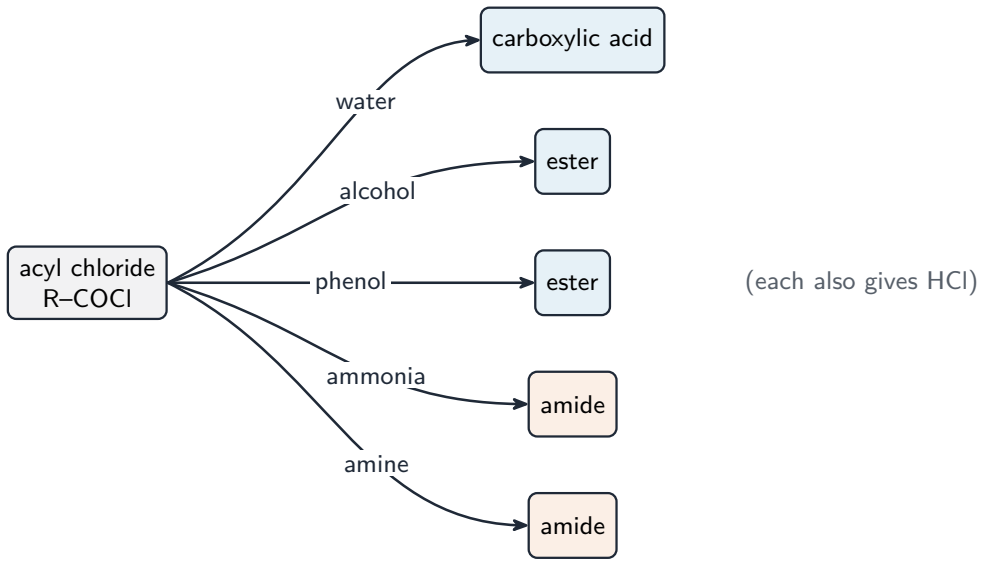
Build the skills to answer exam questions on **acyl chlorides** 酰氯 — their reactions, the **addition–elimination** 加成消去 mechanism, and the order of ease of **hydrolysis** 水解.

You must be able to:

- give the products of an acyl chloride with water, alcohols, phenol, ammonia and amines
- describe the addition–elimination mechanism
- explain the order acyl chloride ≫ alkyl chloride ≫ aryl chloride

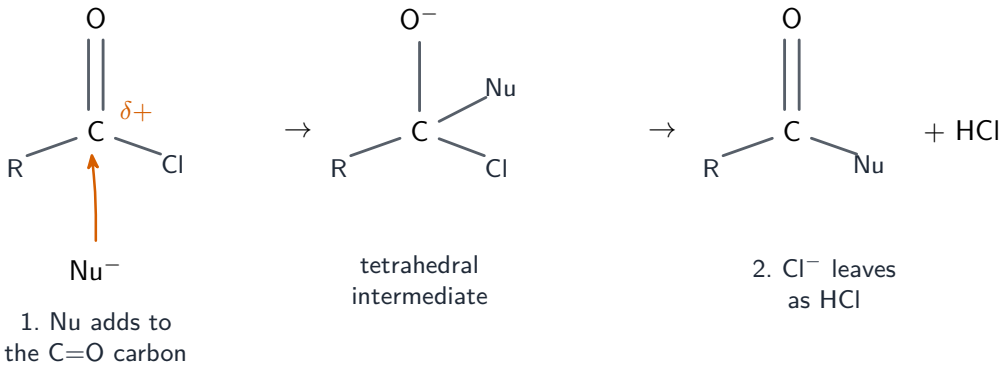
1 Worked examples

■ Reactions and mechanism



Acyl chlorides are very reactive: with water, an alcohol, phenol, ammonia or an amine they give the labelled product + HCl

Reactant	Product (+ HCl)
water	carboxylic acid
alcohol / phenol	ester
ammonia	amide
amine	(N-substituted) amide



Addition–elimination: the nucleophile adds to the δ+ carbonyl carbon, then C=O reforms and Cl^- leaves as HCl

■ Acyl chlorides: one mechanism, five nucleophiles

An **acyl chloride** 酰氯 RCOCl is the most reactive carboxylic acid derivative, because chloride is a good leaving group and the carbonyl carbon carries a large $\delta+$ (both the oxygen and the chlorine withdraw electrons).

Every reaction is the same mechanism: addition–elimination 加成消去.

1. The nucleophile's lone pair attacks the $\delta+$ carbonyl carbon.
2. The C = O π bond breaks, and the electrons go onto the oxygen — a tetrahedral intermediate with a negative oxygen.
3. The oxygen re-forms the double bond and **expels the chloride ion**.
4. A proton is lost from the attacking group, and HCl leaves (visible as **steamy white fumes**).

Nucleophile	Product	Note
water	carboxylic acid	vigorous, steamy fumes of HCl
an alcohol	**ester**	better than esterification: fast, and it goes to completion
ammonia	primary **amide**	
a primary amine	N-substituted amide	
phenol	aryl ester	phenol is too weak a nucleophile for a carboxylic acid, so this route is needed

Worked example. Give the product and the mechanism type when ethanoyl chloride

reacts with methylamine, and explain why the reaction is faster than the corresponding reaction of ethanoic acid.

1. Product: $CH_3CONHCH_3$, N-methylethanamide, plus HCl.
2. Mechanism: nucleophilic addition–elimination.
3. Faster because the chloride is a much better leaving group than the $-OH$ of the acid, and the carbonyl carbon in the acyl chloride is more $\delta+$, so it is attacked more readily.

△ **Draw the arrows from the lone pair, and show the intermediate.** The intermediate with the negatively charged oxygen is a mark on its own, and so is the arrow that expels the chloride.

2 Practice

2.1 Name the product when ethanoyl chloride reacts with water. [1]

2.2 Name the type of mechanism by which acyl chlorides react. [1]

2.3 Give the organic product when propanoyl chloride reacts with ethanol. [1]

2.4 State the observation when an acyl chloride is added to water. [2]

2.5 Explain why acyl chlorides are more reactive than carboxylic acids towards nucleophiles. [2]

3 Exam-style questions

3.1 Ethanoyl chloride reacts with ammonia to give: [1]

- **A** an ester
- **B** ethanamide
- **C** ethanoic acid
- **D** an amine

3.2 Which order of ease of hydrolysis is correct? [1]

- **A** aryl chloride ≫ alkyl chloride ≫ acyl chloride
- **B** acyl chloride ≫ alkyl chloride ≫ aryl chloride
- **C** alkyl chloride ≫ acyl chloride ≫ aryl chloride
- **D** they hydrolyse equally easily

3.3 Describe the **addition–elimination** mechanism for the reaction of ethanoyl chloride with an alcohol. [3]

3.4 Explain why an acyl chloride is hydrolysed far more easily than an aryl chloride (e.g. chlorobenzene). [2]

3.5 Ethanoyl chloride, CH_3COCl, reacts with a range of nucleophiles.

(a) Complete the table by naming the organic product of each reaction. [4]

Nucleophile	Organic product
water	
methanol	
ammonia	
phenol	

(b) Draw the mechanism for the reaction with ammonia, showing curly arrows and the intermediate. [4]

(c) Name the type of mechanism. [1]

(d) Explain why an ester is better prepared from an acyl chloride than from the corresponding carboxylic acid. [3]

(e) Suggest why phenol reacts with ethanoyl chloride but not appreciably with ethanoic acid. [2]

Solutions

2.1 ethanoic acid.

2.2 addition–elimination (nucleophilic).

2.3 Ethyl propanoate.

2.4 A vigorous reaction; steamy white fumes of hydrogen chloride are produced.

2.5 Chloride is a much better leaving group than the hydroxyl of an acid; and the carbonyl carbon is more $\delta+$ because both the oxygen and the chlorine withdraw electrons, so it is attacked more readily.

3.1 B. Acyl chloride + ammonia $\rightarrow$ amide (ethanamide) + HCl.

3.2 B. Acyl chloride $\gg$ alkyl chloride $\gg$ aryl chloride.

3.3 the nucleophile (the alcohol's O lone pair) adds to the slightly positive carbonyl carbon, forming a tetrahedral intermediate; the C=O double bond reforms; the C–Cl bond breaks and HCl is eliminated, giving the ester.

3.4 the carbonyl carbon of an acyl chloride is strongly $\delta+$ and easily attacked by a nucleophile; in an aryl chloride the C–Cl bond is strengthened by overlap with the ring and the ring repels nucleophiles, so it resists hydrolysis.

3.5 (a) Ethanoic acid; methyl ethanoate; ethanamide; phenyl ethanoate.
(b) Curly arrow from the nitrogen's lone pair to the $\delta+$ carbonyl carbon; arrow from the C = O π bond onto the oxygen, giving the tetrahedral intermediate with a negative oxygen; arrow from the oxygen re-forming the double bond, with a second arrow expelling the chloride ion; loss of a proton to give ethanamide, and HCl.
(c) Nucleophilic addition–elimination.
(d) The reaction with an acyl chloride is fast and goes essentially to completion; esterification of a carboxylic acid is slow, needs an acid catalyst and reaches an equilibrium, so the yield is limited; the acyl chloride route therefore gives a higher yield in less time.
(e) Phenol is a weak nucleophile because its oxygen lone pair is delocalised into the ring; the acyl chloride is reactive enough to be attacked even by a weak nucleophile, whereas the far less reactive carboxylic acid is not.

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.

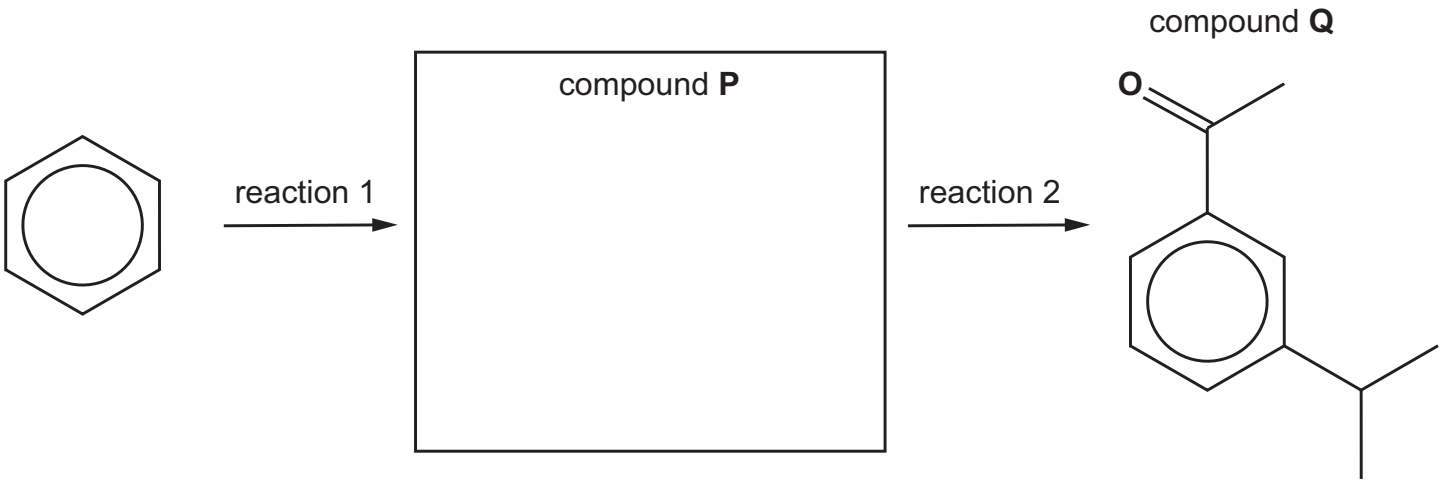


Fig. 8.1

(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 C_6H_5Br and $C_6H_5CH_2Br$ are added to warm $AgNO_3(aq)$.

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

C_6H_5Br with $AgNO_3(aq)$ .....

$C_6H_5CH_2Br$ with $AgNO_3(aq)$ .....

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, RCOC*l*.

(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.

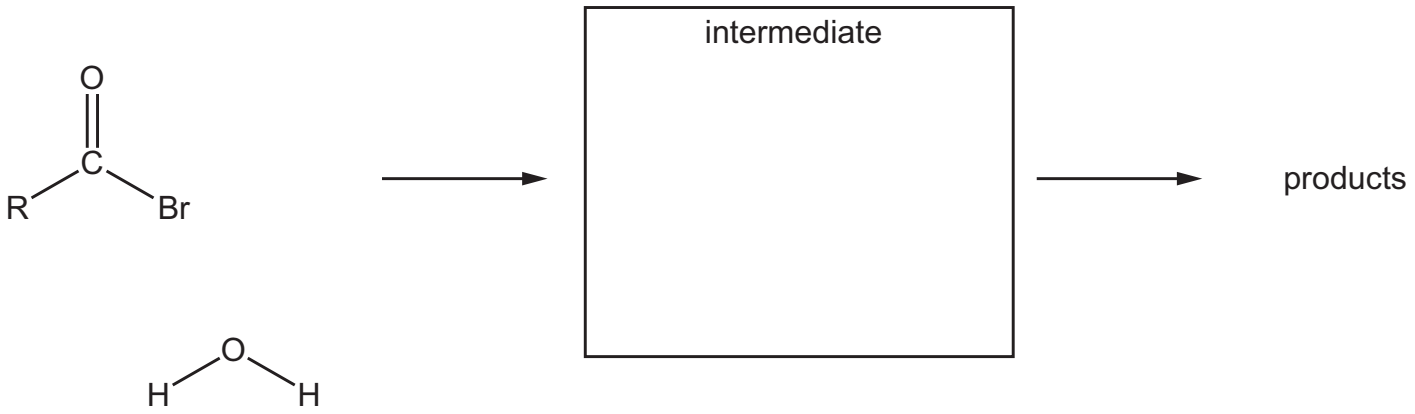


Fig. 8.2

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

(a) Define isoelectric point.

.....

..... [1]

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

asparagine at pH 2	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.

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

[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.

..... [1]

(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**, $C_{11}H_{16}N_4O_8$

[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, $HOOCCH(NH_2)CH_2CONH_2$, 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.

[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.