33. Carboxylic acids and derivatives

33.3 Acyl chlorides

Paper 4

Question Paper

1 **(d)** $C_6H_5CONH_2$ is formed by reacting benzoyl chloride, C_6H_5COCl, with NH_3.

Complete the mechanism in Fig. 8.1 for the reaction of C_6H_5COCl with NH_3.

Include all relevant lone pairs of electrons, curly arrows, charges and dipoles. Draw the structure of the organic intermediate.

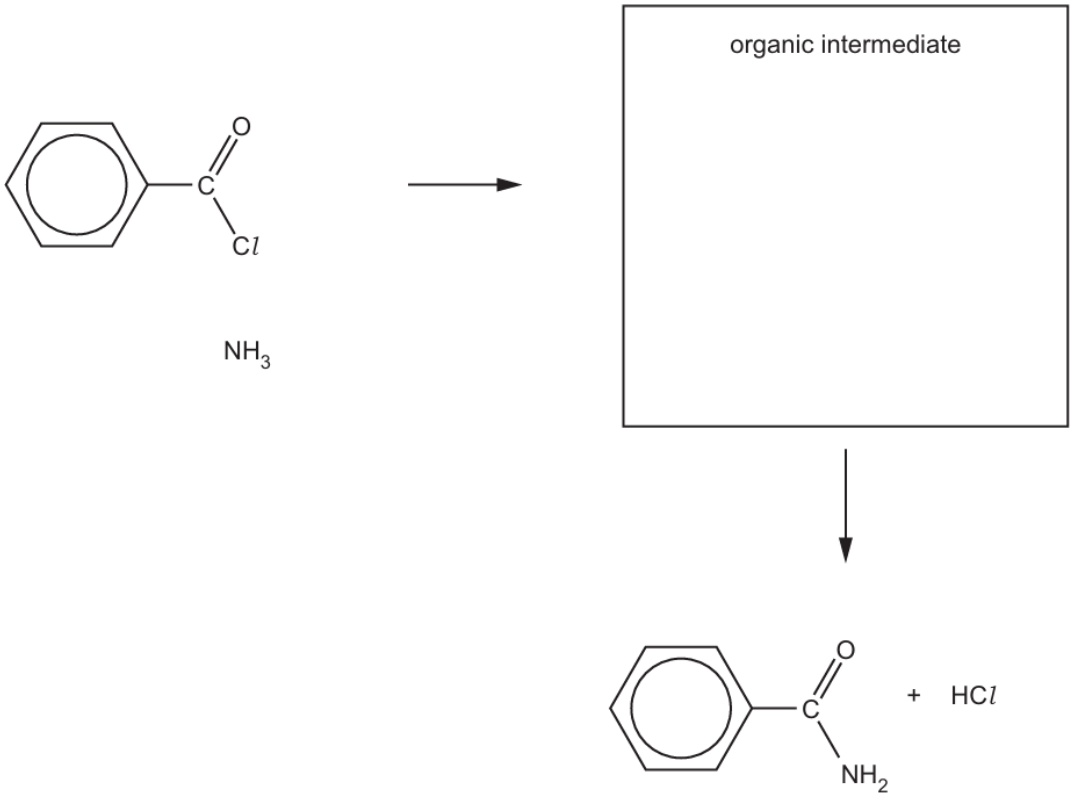


Fig. 8.1

[4]

2 **(b)** Acyl chlorides are formed by reacting carboxylic acids with thionyl chloride, $SOCl_2$.

(i) Ethanedioyl chloride, $(COCl)_2$, can be prepared by reacting ethanedioic acid, $(COOH)_2$, with an excess of $SOCl_2$.

Write an equation for this reaction.

..... [1]

(ii) Samples of $(COCl)_2$ are reacted separately with an excess of warm acidified $KMnO_4(aq)$ and with $H_2NCH_2CH_2NH_2$.

The carbon-containing product from the reaction with $H_2NCH_2CH_2NH_2$ has the molecular formula $C_4H_6N_2O_2$.

Complete the boxes in Fig. 9.1 to suggest the structure of the carbon-containing product in each reaction.

with warm acidified $KMnO_4(aq)$	with $H_2NCH_2CH_2NH_2$

Fig. 9.1

[2]

3 Fig. 6.1 shows two reactions of ethanedioic acid, HOOCCOOH.

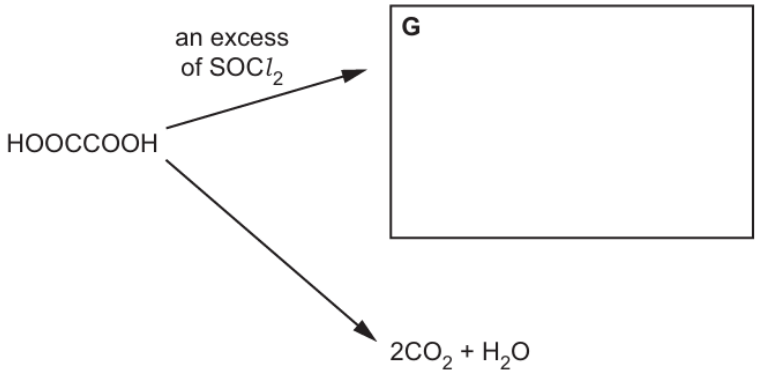


Fig. 6.1

(a) (i) Draw the organic product **G** in the box in Fig. 6.1.

[1]

(ii) In Fig. 6.1, $SOCl_2$ is given as the reagent that reacts with HOOCCOOH to produce **G**.

Identify a different reagent that also reacts with HOOCCOOH to produce **G**.

..... [1]

4 **(d)** Acyl bromides, RCOBr, can be synthesised by the reaction of a carboxylic acid and $SOBr_2$.

This is a similar reaction to the synthesis of acyl chlorides using $SOCl_2$.

(i) Give an equation for the reaction between ethanoic acid and $SOBr_2$.

..... [1]

(ii) Suggest the relative ease of hydrolysis of acyl bromides, RCOBr, acyl chlorides, RCOCl, and alkyl chlorides, RCl.

Explain your answer.

..... > ..... > .....
easiest to hydrolyse hardest to hydrolyse

.....

.....

.....

.....

.....
[3]

5 **(b)** C_6H_5COCl reacts with phenol, C_6H_5OH, to give the ester phenyl benzoate, $C_6H_5COOC_6H_5$.

An incomplete description of the mechanism of this reaction is shown in Fig. 9.1.

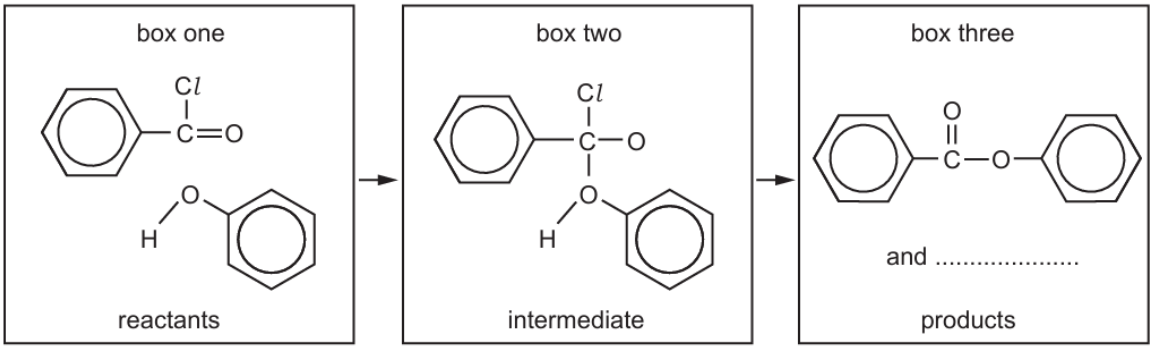


Fig. 9.1

(i) Complete the mechanism in Fig. 9.1 and include:

- all relevant dipoles (δ+ and δ–) and full electric charges (+ and –) on the species in box one and in box two
- all relevant lone pairs on the species in box one and in box two
- all relevant curly arrows to show the movement of electron pairs in box one and in box two
- the formula of the second product in box three.

[4]

(ii) Name this mechanism.

..... [1]

(c) Benzoyl chloride, chlorobenzene and chloroethane differ in their rates of hydrolysis when each compound is added separately to water at 25 °C.

Suggest the relative ease of hydrolysis of these three compounds.

Explain your answer.

....
hardest to hydrolyse easiest to hydrolyse

explanation .....

.....

.....

.....

.....

[3]

6 Benzene can be used to make benzoic acid in the two-step process shown in Fig. 7.1.

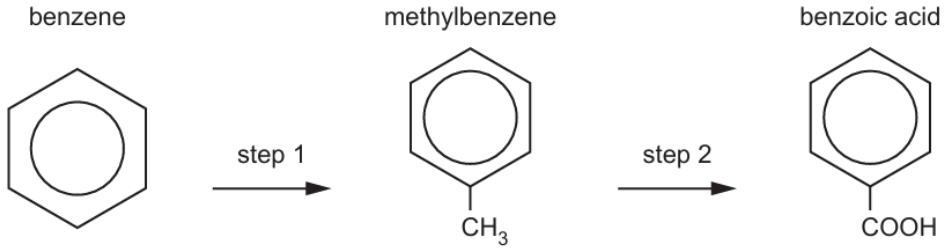
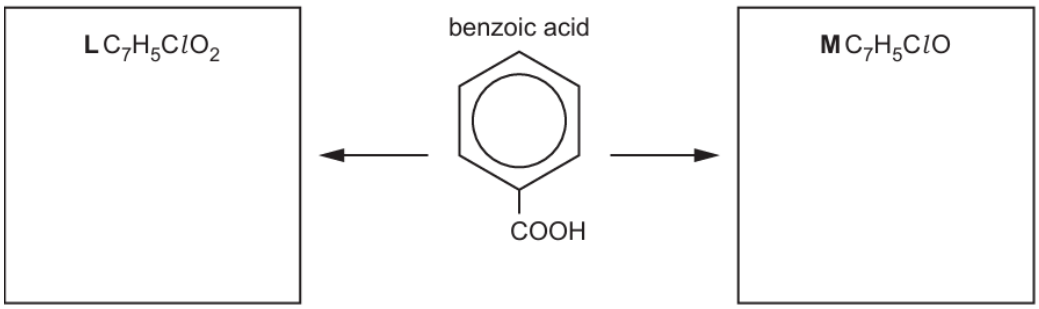


Fig. 7.1

(c) (ii) When treated with a chlorine-containing reagent under suitable conditions, benzoic acid forms compound **L**.

When treated with a **different** chlorine-containing reagent under **different** conditions, benzoic acid forms compound **M**.

Suggest and draw structures of compounds **L** and **M** in the boxes. The molecular formula of each product is given.



State the reagents and conditions to form compound **M** from benzoic acid.

..... [3]

7 **(d)** $CH_3CH_2NHCH_2CH_3$ reacts with ethanoyl chloride, CH_3COCl, to give the amide N,N-diethylethanamide, $CH_3CON(C_2H_5)_2$.

An incomplete description of the mechanism of this reaction is shown in Fig. 9.1.

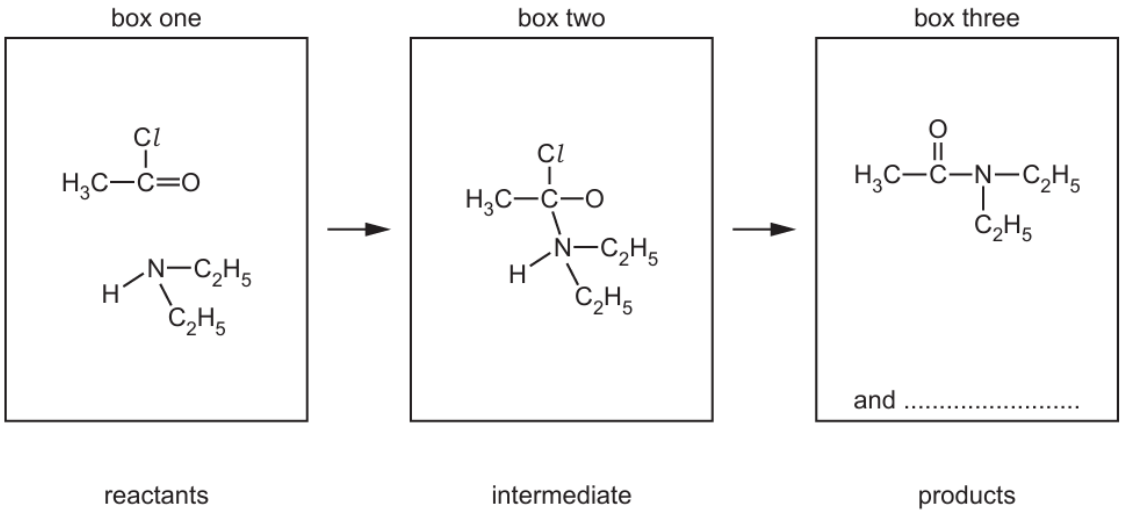


Fig. 9.1

(i) Complete the mechanism in Fig. 9.1. You should include:

- all relevant dipoles (δ+ and δ–) and full electric charges (+ and –) on the species in box one and in box two
- all relevant lone pairs on the species in box one and in box two
- all relevant curly arrows to show the movement of electron pairs in box one and in box two
- the formula of the second product in box three.

[4]

(ii) Name this mechanism.

..... [1]

8 **(c)** **(i)** Benzoyl chloride, C_6H_5COCl, can be synthesised by the reaction of benzoic acid with either PCl_5 or $SOCl_2$.

Complete the equations for these reactions.

reaction 1 $C_6H_5COOH + PCl_5 \rightarrow C_6H_5COCl +$ ..... + ...

reaction 2 $C_6H_5COOH + SOCl_2 \rightarrow C_6H_5COCl +$ ..... + ...

[1]

(ii) Use your answer to **(c)(i)** to suggest why it is easier to isolate, in a pure form, the C_6H_5COCl from reaction 2 compared to reaction 1.

.....

..... [1]

(d) Benzoyl chloride is hydrolysed by water at room temperature to form benzoic acid.

(i) Complete the diagram to show the mechanism for the reaction between C_6H_5COCl and H_2O.

Include charges, dipoles, lone pairs of electrons and curly arrows as appropriate.

[4]

(ii) Name the type of mechanism you showed in **(d)(i)**.

..... [1]

9 The structure of cyclohexylamine is shown in Fig. 9.1.

cyclohexylamine

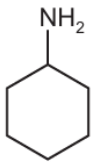


Fig. 9.1

(b) Cyclohexylamine reacts with ethanoyl chloride to form the corresponding amide, **L**.

L

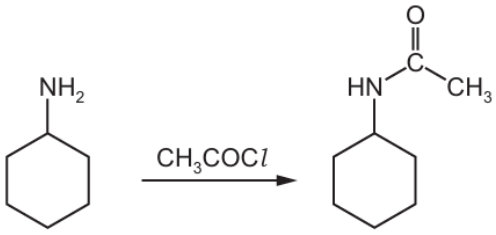


Fig. 9.2

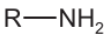
(i) Name the mechanism for the reaction shown in Fig. 9.2.

..... [1]

(ii) Complete the mechanism of the reaction between cyclohexylamine and CH_3COCl.

$R–NH_2$ is used to represent cyclohexylamine.

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



[4]

(iii) The reaction between cyclohexylamine and an excess of CH_3COCl forms compound **M**. Compound **M** has the molecular formula $C_{10}H_{17}NO_2$.

Suggest and draw the structure of **M**.

[1]

10 **(c)** **P** can be used to make compound **R** in a two-step reaction, shown in Fig. 7.2.

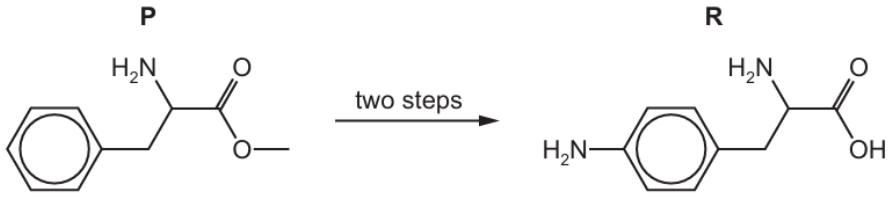


Fig. 7.2

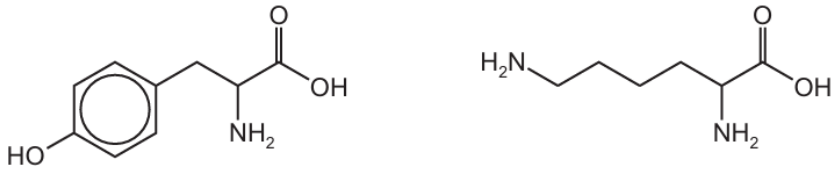
(i) Identify the reagents and conditions used for the two steps of the reaction.

step 1 .....

step 2 .....

[2]

11 Tyrosine and lysine, shown in Fig. 9.1, are naturally occurring amino acids found in proteins.



tyrosine lysine

Fig. 9.1

(b) When ethanoic acid is treated with PCl_5 product **D** is formed.

When **D** is added to tyrosine two different isomeric products, **E** and **F**, are formed.

E has an ester linkage, **F** does not.

Draw the structures of **D**, **E** and **F** in the boxes below.

D **E** **F**

[3]

12 **(a)** State and explain the relative rate of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

..... > ..... > .....

fastest slowest

.....

.....

.....

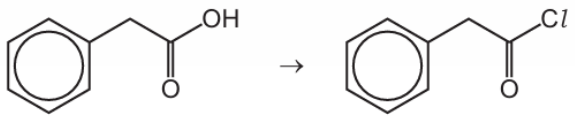
.....

..... [3]

13 Compound **T** is made by a three-stage synthesis.

(a) In stage 1, phenylethanoic acid reacts with a suitable reagent to form compound **R**.

phenylethanoic acid **R**

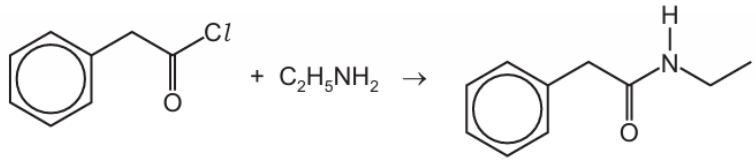
stage 1 

Suggest a suitable reagent for stage 1.

..... [1]

(b) In stage 2, compound **R** reacts with ethylamine to form compound **S**.

R **S**

stage 2 

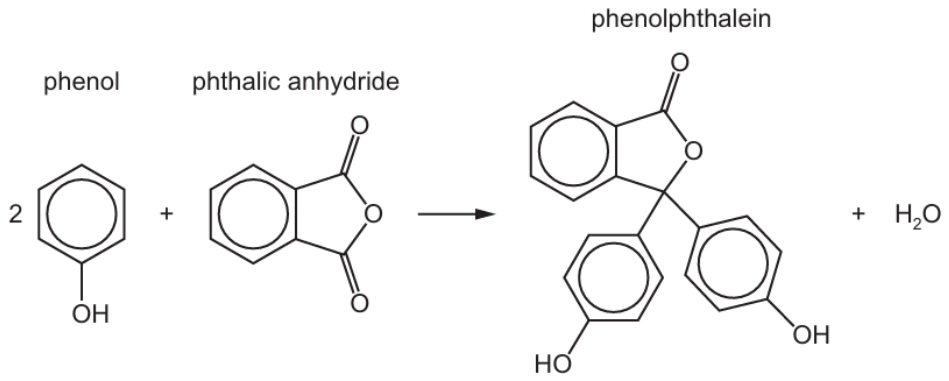
(i) Name the functional group formed in stage 2.

..... [1]

(ii) Identify the other product formed in stage 2.

..... [1]

14 **(c)** The indicator, phenolphthalein, can be synthesised from phthalic anhydride and phenol under certain conditions.



Deduce the *type of reaction* shown by this equation.

..... [1]

15 **(c)** Ethanamide can be made from ethanoic acid in a two-step synthesis.

ethanoic acid $\xrightarrow{\text{step 1}}$ **A** $\xrightarrow{\text{step 2}}$ ethanamide

(i) Compound **A** contains chlorine.

Give the structural formula and name of **A**.

structural formula .....

name .....
[2]

(ii) Suggest suitable reagents for steps 1 and 2.

step 1 .....

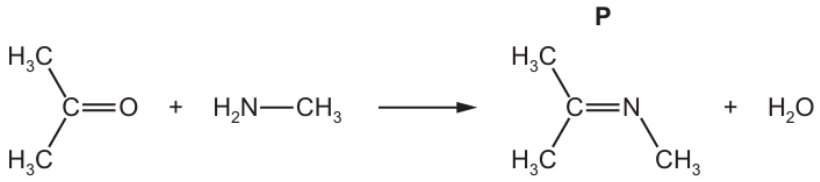
step 2 .....
[2]

16 **(f)** Methylamine is a useful reagent in organic chemistry.

(i) Write an equation for the reaction of ethanoyl chloride with methylamine.

..... [2]

(ii) Methylamine also reacts with propanone to form compound **P** as shown.

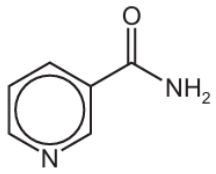


Deduce the *type of reaction* shown here.

..... [1]

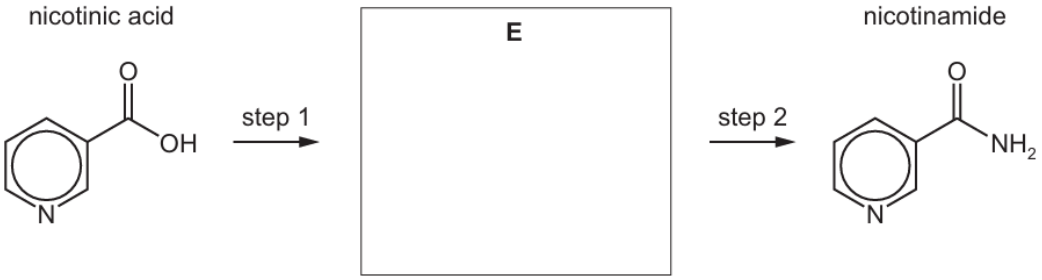
17 The structure of nicotinamide is shown.

nicotinamide



(b) Nicotinamide can be synthesised from nicotinic acid.

The synthesis involves two steps.



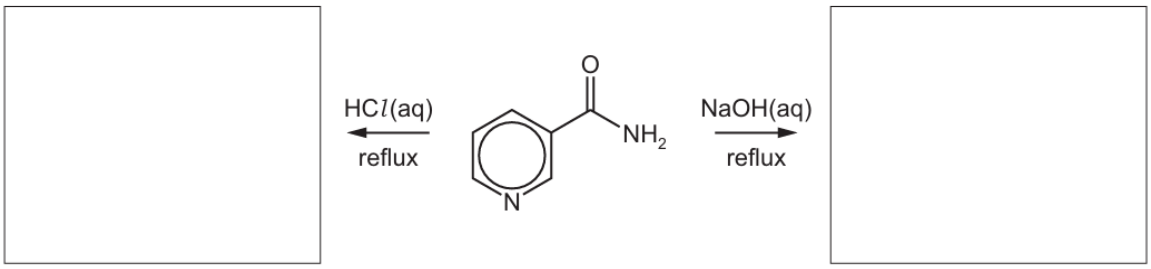
(i) Draw the structural formula of **E** in the box. [1]

(ii) Give the name or formula of a suitable reagent for step 2.

..... [1]

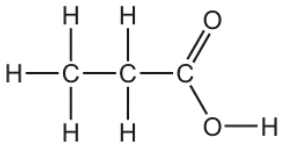
(c) Nicotinamide reacts separately with aqueous acid and aqueous alkali. The six-membered ring remains unchanged in these reactions.

Complete the reaction scheme below to give the structural formula of the organic product of each reaction.

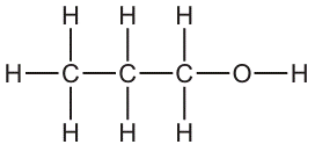


[2]

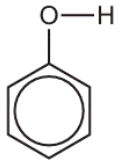
18 The three substances shown all have some acidic properties.



propanoic acid



propan-1-ol



phenol

(d) The ester phenyl propanoate, $C_2H_5CO_2C_6H_5$, can be made from phenol and propanoic acid in a **two-step** synthesis. The first step produces an acyl chloride.

For this **two-step** synthesis,

- draw the structure of the product of the first step,
- state the reagents and conditions needed for each step of the synthesis.

.....

.....

.....

..... [3]