33.3 ACYL CHLORIDES

Learning outcomes

Candidates should be able to:

1. recall the reactions (reagents and conditions) by which acyl chlorides can be produced:
   (a) reaction of carboxylic acids with PCl_3 and heat, PCl_5 or $SOCl_2$
2. describe the following reactions of acyl chlorides:
   (a) hydrolysis on addition of water at room temperature to give the carboxylic acid and HCl
   (b) reaction with an alcohol at room temperature to produce an ester and HCl
   (c) reaction with phenol at room temperature to produce an ester and HCl
   (d) reaction with ammonia at room temperature to produce an amide and HCl
   (e) reaction with a primary or secondary amine at room temperature to produce an amide and HCl
3. describe the addition–elimination mechanism of acyl chlorides in reactions in 33.3.2(a)–(e)
4. explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides, and halogenoarenes (aryl chlorides

Introduction

To generalise the reactions of acyl chlorides, we can write:

ROCl + HZ → ROZ + HCl

where HZ can be water, an alcohol, phenols, ammonia or an amine.

https://www.youtube.com/watch?v=KgYAvLNqBmU

Hydrolysis

1. 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.

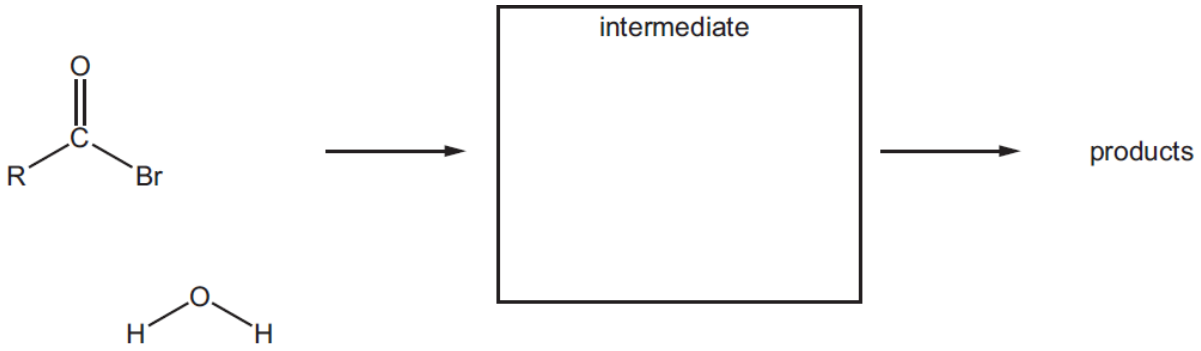
   (ii) Name the type of mechanism you showed in **(i)**.

   ..... [1]

2. 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.

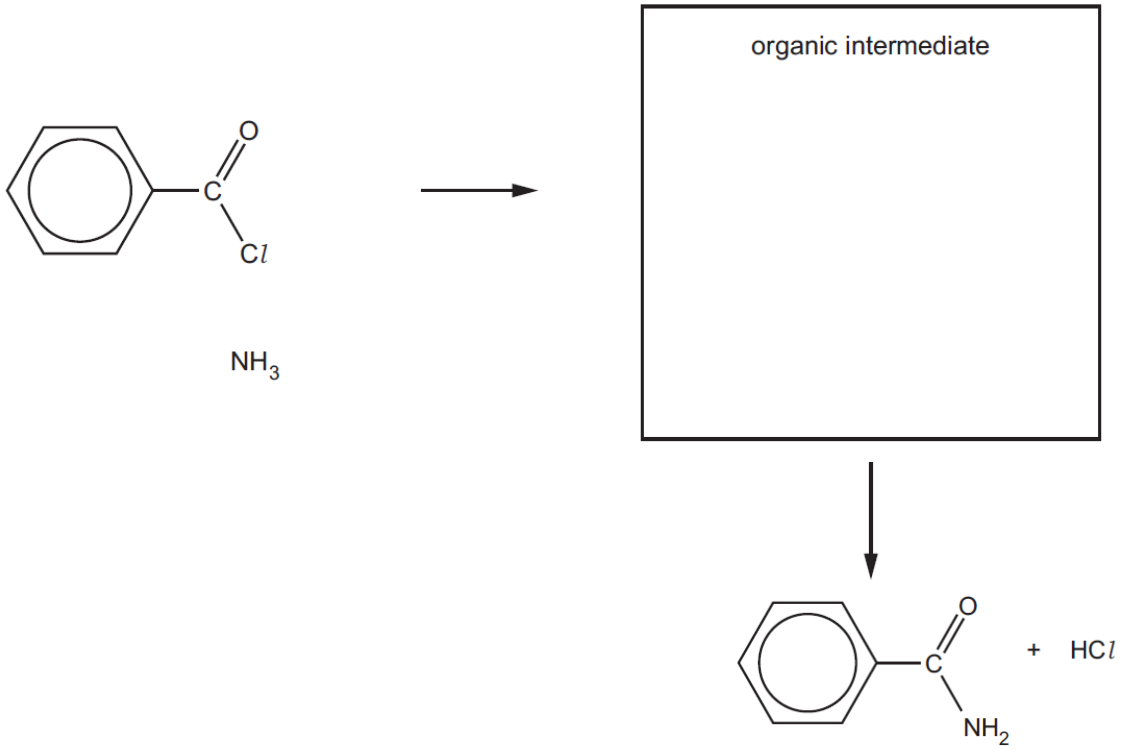
   ..... [1]

(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.



Reaction with ammonia

3. $C_6H_5CONH_2$ 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. [4]



4. Cyclohexylamine reacts with ethanoyl chloride to form the corresponding amide, **L**.

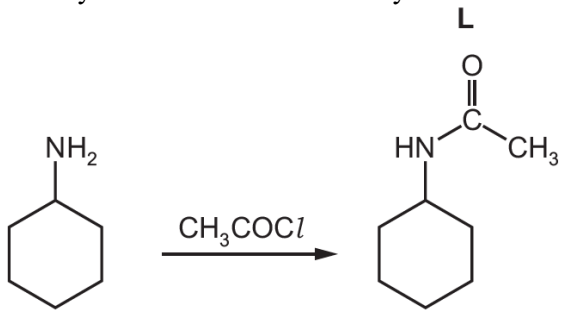


Fig. 9.2

(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]

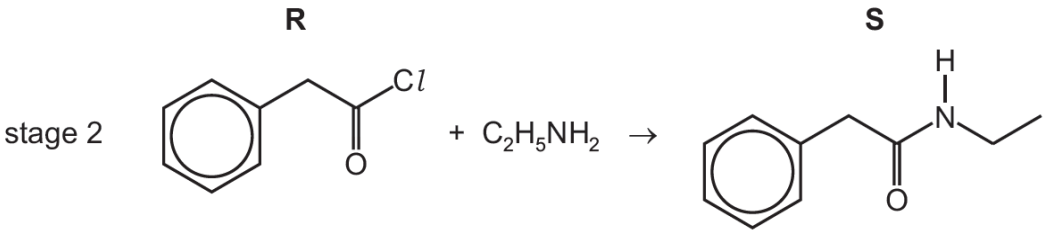
5. Samples of $(COCl)_2$ are reacted separately with an excess of warm acidified $KMnO_4(aq)$ and with $H_2NCH_2CH_2NH_2$.
The carbon-containing product from the reaction with $H_2NCH_2CH_2NH_2$ has the molecular formula $C_4H_6N_2O_2$.
Complete the boxes in Fig. 9.1 to suggest the structure of the carbon-containing product in each reaction.

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

Fig. 9.1

[2]

6. In stage 2, compound R reacts with ethylamine to form compound S.



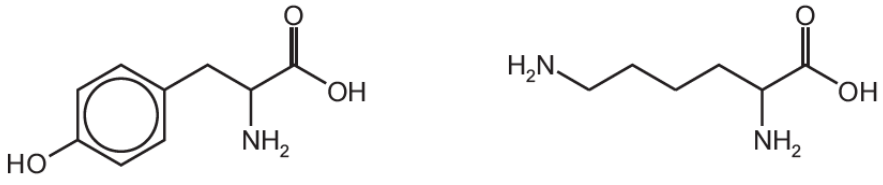
(i) Name the functional group formed in stage 2.

..... [1]

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

..... [1]

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



tyrosine lysine

Fig. 9.1

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]

Reaction with secondary amines

8. $(CH_3CH_2)_2NH$ reacts with ethanoyl chloride, CH_3COCl.
Complete the equation for this reaction.

$(CH3CH_2)_2NH$ + CH3COCl ..... [1]

9. $CH_3CH_2NHCH_2CH_3$ reacts with ethanoyl chloride, CH_3COCl, to give the amide N,N-diethylethanamide, $CH_3CON(C_2H5)_2$.
An incomplete description of the mechanism of this reaction is shown in Fig. 9.1.

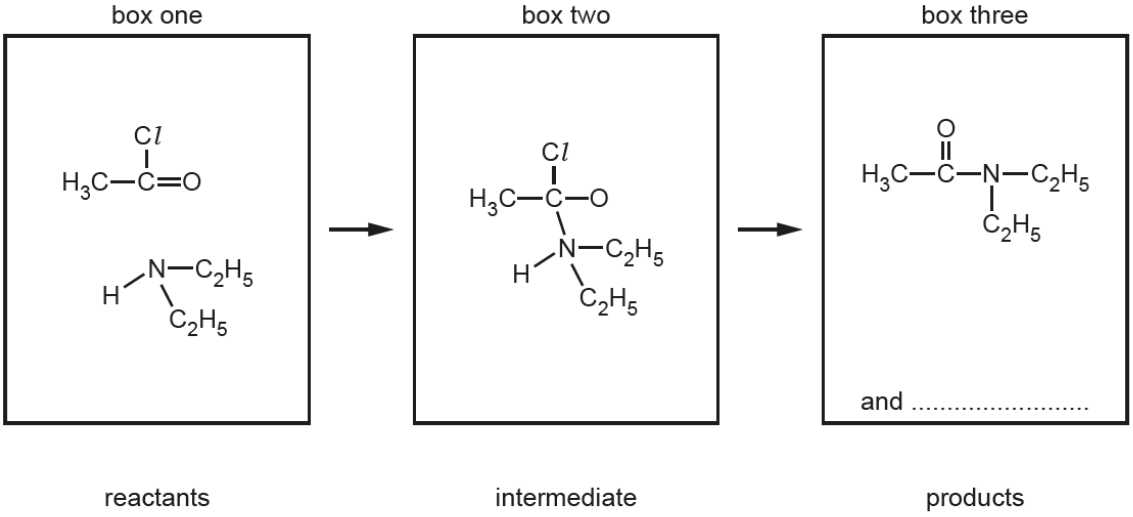


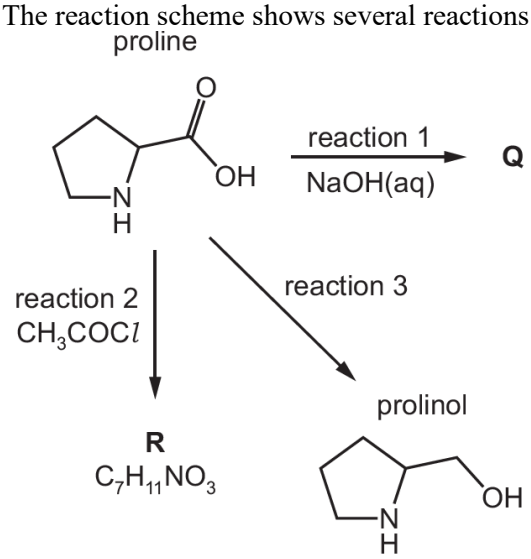
Fig. 9.1

(i) Complete the mechanism in Fig. 9.1. You should include:
- all relevant dipoles ($\delta+$ and $\delta-$) 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]

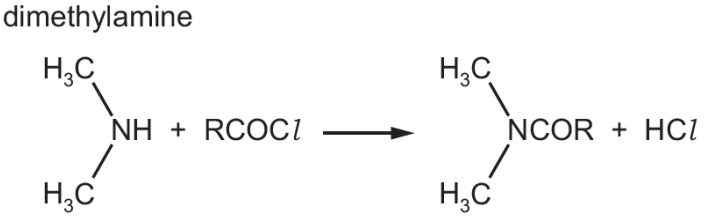
10. The reaction scheme shows several reactions of proline.



(i) Write an equation for the reaction of proline with NaOH(aq) in reaction 1.

$C_4H_7NHCO_2H$ + …… [1]

(ii) Proline has a secondary amine functional group.
Secondary amines react with acyl chlorides. For example, dimethylamine reacts with RCOC*l* according to the following equation.



Suggest the skeletal structure of **R**, $C_7H_{11}NO_3$, the product of reaction 2.[1]

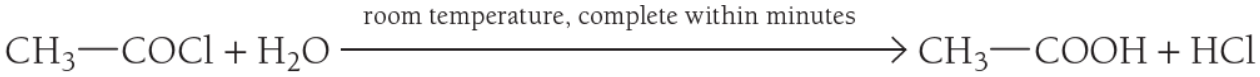
(iii) Suggest the reagent required for reaction 3.

..... [1]

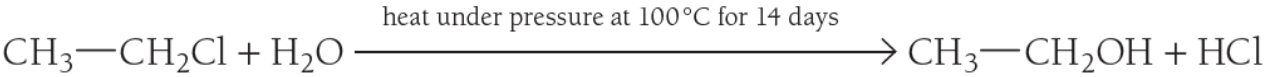
Relative ease of hydrolysis

The electronegativity of oxygen and the easily polarised C=O double bond have a dramatic effect on the reactivity of acyl chlorides compared with that of chloroalkanes.

Acyl chlorides react readily with water:



Compare this with the conditions for the hydrolysis of a halogenoalkane:

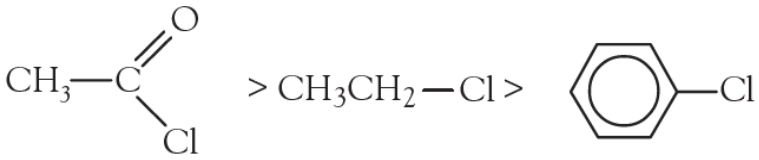


As a result of the speedy reaction with water, acyl chlorides produce steamy fumes of HCl(g) when a few drops of water are added to them. This is a good test for them.

Together with what we have already seen in Sections 16.3 and 27.4, we note that in the reaction:

R¬Cl + H2O → R¬OH + HCl

the relative rates of hydrolysis are as follows:



The ease of hydrolysis, starting with the compounds most readily broken down, is:

acyl chloride > chloroalkane > aryl chloride or chloroarene

11. State and explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides.

    ..... , ... , ...

    easiest to hydrolyse hardest to hydrolyse

    .....

    .....

    .....

    .....

    ..... [3]

12. Suggest the relative ease of hydrolysis of acyl bromides, RCOBr, acyl chlorides, RCOC*l*, and alkyl chlorides, RC*l*. Explain your answer.

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

    easiest to hydrolyse hardest to hydrolyse

    .....

    .....

    .....

    .....

    ..... [3]

13. 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 .....

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..... [3]

14. Describe the difference in reactivity between ethanoyl chloride and chlorobenzene with water.
Explain your answer.

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..... [2]

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

..... > ..... > .....
fastest slowest

.....

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..... [3]

*****This is not a complete note. It is just to guide you. It is recommended to study the prescribed textbooks along with this material. *****