Cambridge

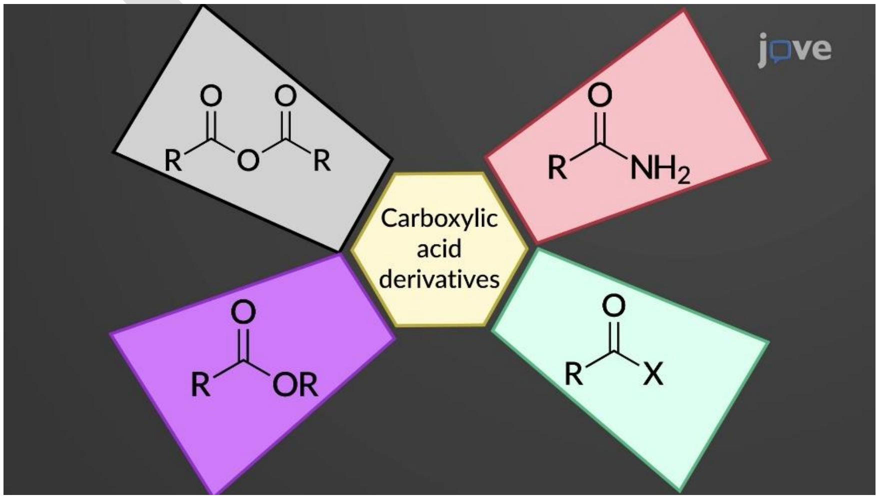
A2 Level

Chemistry

CODE: (9701)

Chapter 26

Carboxylic acids and their derivatives

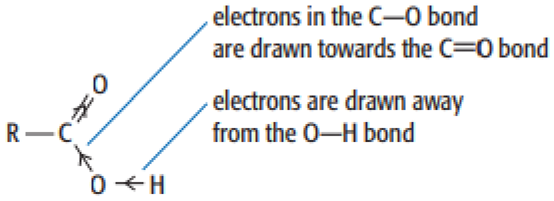


Carboxylic acids react with excess H+(aq) ions in their solutions, forming carboxylates like sodium ethanoate. They are weak acids, with most molecules undissociated in water, and their typical reactions include base-water reactions.

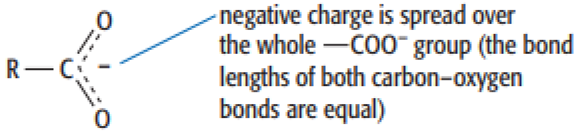
$$\underset{\text{ethanoic acid}}{CH_3COOH(aq)} \rightleftharpoons \underset{\text{ethanoate ion}}{CH_3COO^-(aq)} + H^+(aq)$$

The carboxylic acids are stronger acids than alcohols.

■The O--H bond in the carboxylic acid is weakened by the carbonyl group, C= O.



■The carboxylate ion is stabilised by the delocalisation of electrons around the ---COO– group. This delocalisation spreads out the negative charge on the carboxylate ion, reducing its charge density and making it less likely to bond with an H+(aq) ion to re-form the undissociated acid molecule



Electron-withdrawing groups bonded to the carbon atom next to the COOH group make the acid stronger. There are two reasons for this:

■Electron-withdrawing groups further weaken the O---H bond in the undissociated acid molecule

■Electron-withdrawing groups extend the delocalisation of the negative charge on the ----COO– group of the carboxylate ion, further increasing the stabilising of the ---COO– group and making it less likely to bond with an H+(aq) ion.

CCl3COOH, a trichloroethanoic acid, is the strongest due to its three electron-negative Cl atoms, which weaken the O-H bond and stabilize the resulting anion, making it less attractive to H+(aq) ions.

Acid	**K_a at 25 °C / mol dm^{-3}**
ethanoic acid, CH_3COOH	1.7×10^{-5}
chloroethanoic acid, $CH_2ClCOOH$	1.3×10^{-3}
dichloroethanoic acid, $CHCl_2COOH$	5.0×10^{-2}
trichloroethanoic acid, CCl_3COOH	2.3×10^{-1}

Table 26.1 The larger the value of K_a, the stronger the acid.

Ethanoic acid is the weakest acid in Table 26.1, as the methyl group is electron donating. This has the opposite effect to electron-withdrawing groups:

■It strengthens the O H bond in the acid's -----COOH group

■It donates negative charge towards the ----COO– group of the carboxylate ion, making it more likely to accept an H+(aq) ion

Oxidation of two carboxylic acids

However, methanoic acid (HCOOH) is a stronger reducing agent than other carboxylic acids, so it can undergo further oxidation.

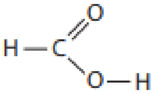


Figure 26.3 The displayed formula of methanoic acid.

The half-equation for the oxidation of methanoic acid can be written in terms of electron transfer to an oxidising agent as:

$$\text{oxidation number} \quad \underset{+2}{\text{HCOOH}} \xrightarrow{\text{oxidation}} \underset{+4}{\text{CO}_2} + 2\text{H}^+(aq) + 2e^-$$

or in terms of the addition of oxygen from an oxidising agent as:

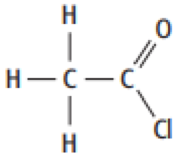
$$\text{HCOOH} + [\text{O}] \longrightarrow \text{CO}_2 + \text{H}_2\text{O}$$

Methanoic acid can be oxidized by stronger oxidising agents like potassium manganate or potassium dichromate, decolorizing purple or orange solutions, and ethanedioic acid, a dicarboxylic acid with a molecular formula of $H_2C_2O_4$.

Acyl chlorides

Making acyl chlorides

The displayed formula of ethanoyl chloride is:



ethanoyl chloride

Reactions of acyl chlorides

Many useful compounds can be synthesised from carboxylic acids. However, the synthetic reactions that are needed can be difficult to do because carboxylic acids are quite unreactive. One way round this is to first convert the carboxylic acid into an **acyl chloride.**

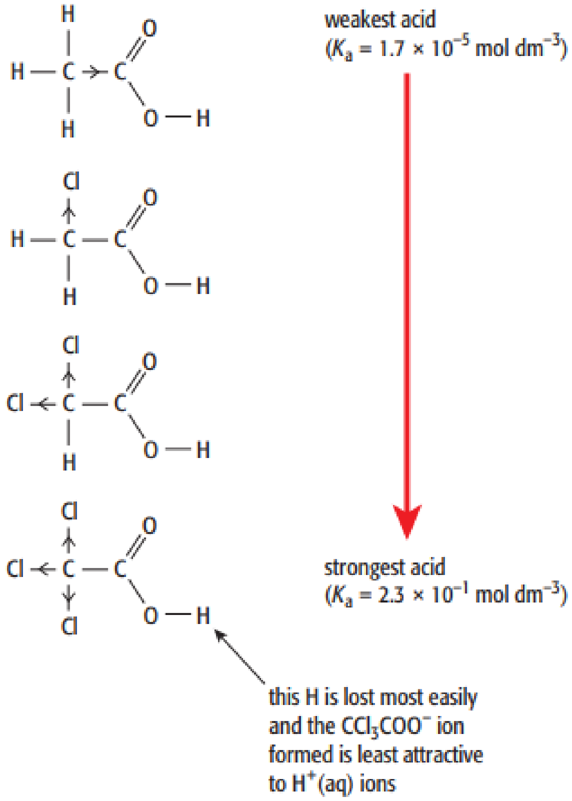


Figure 26.2 The more electron-withdrawing groups on the C atom in the COOH group, the stronger the acid.

The structural formula of ethanoyl chloride can be written as CH_3COCl.

We can prepare acyl chlorides from their corresponding carboxylic acid using phosphorus(V) chloride, phosphorus(III) chloride or sulfur dichloride oxide ($SOCl_2$).

With phosphorus(V) chloride:

$$CH_3COOH + PCl_5 \longrightarrow CH_3COCl + POCl_3 + HCl$$

No special conditions are required for this reaction.

With phosphorus(III) chloride:

$$3CH_3COOH + PCl_3 \longrightarrow 3CH_3COCl + H_3PO_3$$

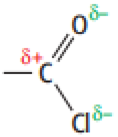
Heat is required for this reaction.

With sulfur dichloride oxide:

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$$

No special conditions are required for this reaction.

Acyl chlorides are reactive compounds. The carbonyl carbon has electrons drawn away from it by the Cl atom as well as by its O atom, and both are strongly electronegative atoms. This gives the carbonyl carbon a relatively large partial positive charge and makes it particularly open to attack from nucleophiles.



The structural formulae of benzoic acid and its derivative benzoyl chloride are shown in Figure 26.5.

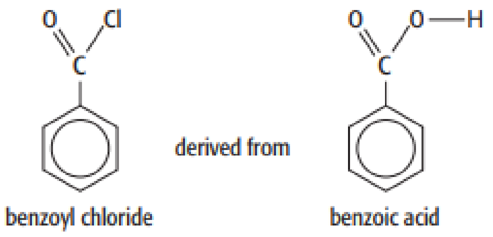


Figure 26.5 Benzoyl chloride is the acyl chloride derived from benzoic acid.

Figure 26.6 shows the mechanism of the hydrolysis, showing the initial attack by a water molecule, acting as a nucleophile, followed by the elimination of a molecule of hydrogen chloride.

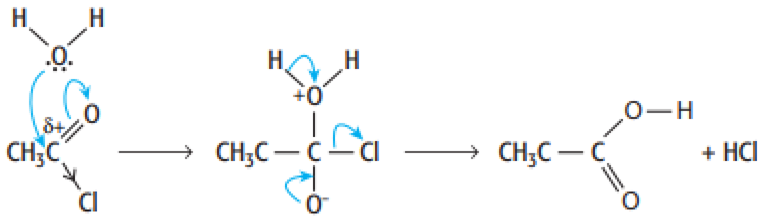
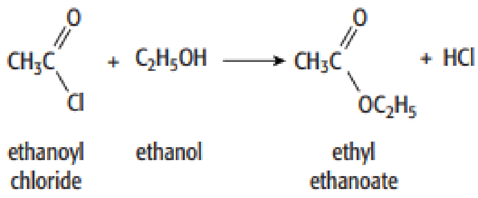


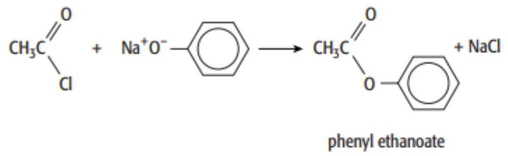
Figure 26.6 The condensation (addition-elimination) mechanism of hydrolysis of ethanoyl chloride.

Hydrolysis is a condensation reaction involving water addition and elimination of a small molecule, such as HCl. It is more vigorous than chloroalkane hydrolysis, which requires a strong alkali like sodium hydroxide. A neutral water molecule can hydrolyze an acyl chloride quickly at room temperature due to the carbon bonded to the chlorine atom being less strongly δ+. Aryl chlorides, like chlorobenzene, do not undergo hydrolysis due to the stronger C-Cl bond character.

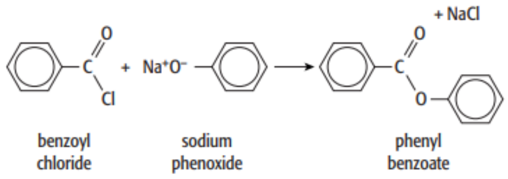
Reaction with alcohols and phenol

Ethanoyl chloride will react vigorously with ethanol to form an ester:



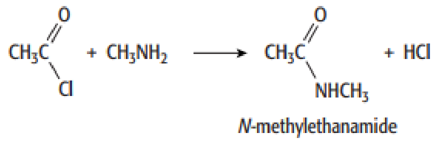


Phenol reacts with acyl chloride when warmed, requiring a base for phenyl esters. The initial reaction creates C6H₅O–, a phenoxide ion, acting as a nucleophile.



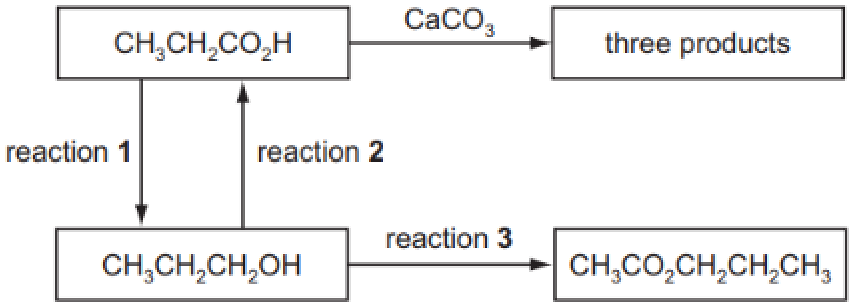
Reaction with amines

Amines contain nitrogen atoms with a lone pair of electrons. This lone pair of electrons is available to attack the carbonyl carbon atom in acyl chlorides. The reaction is vigorous and the organic product is a substituted amide.



Revision questions

1) A series of reactions based on propanoic acid is shown



(a) Write an equation for reaction 1, using [H] to represent the reducing agent

(b) (i) What type of reaction is reaction 2?

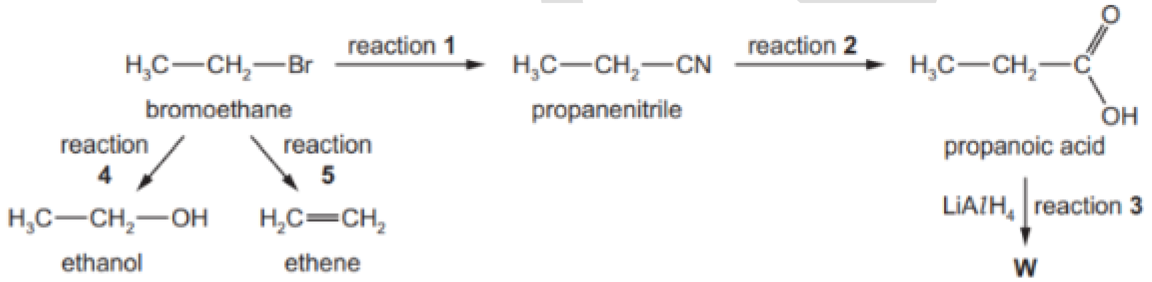
(ii) Suggest a suitable reagent and conditions for reaction 2.[2]

(c) Write an equation for the reaction of propanoic acid with calcium carbonate, $CaCO_3$

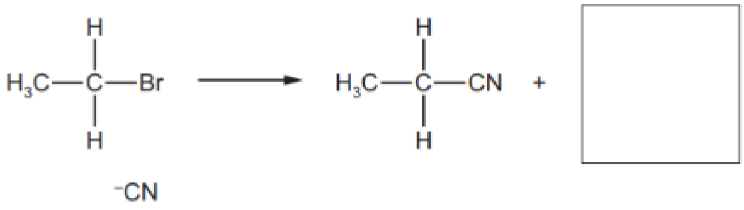
(d) (i) Suggest a suitable reagent and conditions for reaction 3?

(ii) Identify the other product of reaction 3

2) A reaction sequence is shown



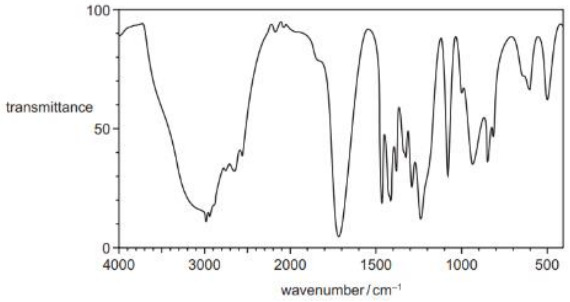
(a) Complete the diagram to show the mechanism of reaction 1. Include all necessary charges, partial charges, lone pairs and curly arrows.



b) (i) Give the name of the type of reaction involved in reaction 3.

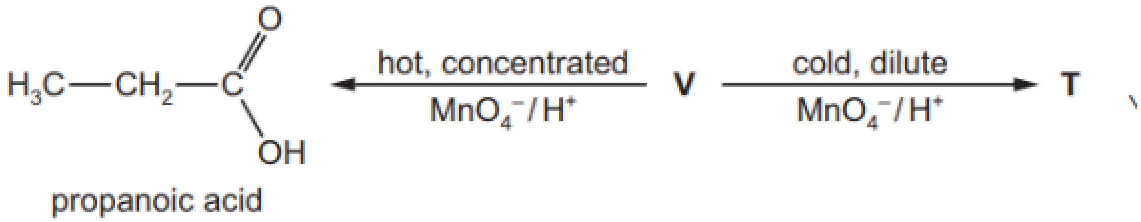
The infra-red spectrum of the propanoic acid produced by reaction 2 is shown.

(ii) Describe and explain the main difference between the infra-red spectrum of W and that of propanoic



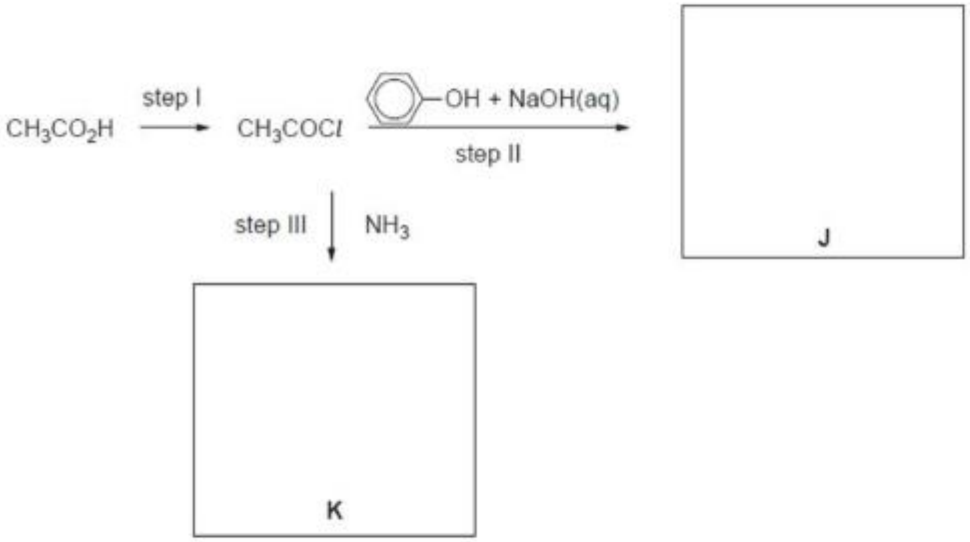
(c) (i) Reactions 4 and 5 use the same reagent.
Give the reagent and conditions needed for reaction 4.
reagent
conditions[2]
(ii) Give the conditions needed for reaction 5.[1]
(d) Under appropriate conditions, ethanol and propanoic acid undergo a condensation reaction.
(i) State the condition necessary for the reaction.[1]
(ii) Draw the skeletal formula of the organic product of this reaction.[1]
(iii) Name the organic product of this reaction.[1]

(e) V reacts with acidified manganate(VII) ions in two different ways depending on the conditions, as shown in the reaction sequence below



V decolourises bromine water.
When the acidified manganate(VII) is hot and concentrated, propanoic acid is the only organic product.
When the acidified manganate(VII) is cold and dilute, the organic product is T which has two chiral centres.
(i) Give the structural formulae of V and T.
ii) Identify the types of stereoisomerism shown by V and T.

3)(a) Acyl chlorides are useful intermediates for making various acid derivatives. The following reaction scheme shows some of the reactions of ethanoyl chloride.



(ii) Write an equation showing the reaction between phenol and NaOH(aq), the reagents in step II.
(iii) Draw the structural formulae of products J and K in the boxes above.

(b) The diacid L occurs naturally and is used as a food additive to enhance the acidic flavour in some fruit drinks.

$HO_2CCH_2CH_2CO_2H$

L

When the diacyl chloride of L is reacted with $HOCH_2CH_2OH$, a polymer is formed.

(i) What type of polymerisation is occurring here?

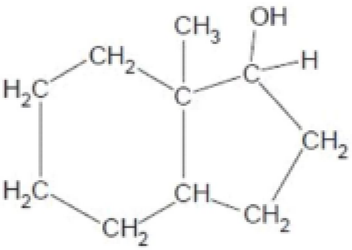
(ii) Write an equation showing the reaction between one mole of the diacyl chloride of L and two moles of $HOCH_2CH_2OH$.

(c) The following formula represents a section of another polymer.

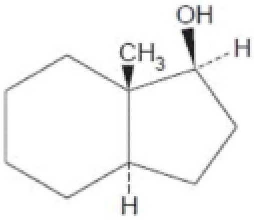
(i) What type of polymer is this?

(ii) Draw the structural formula of each of the monomers that make up this polymer.

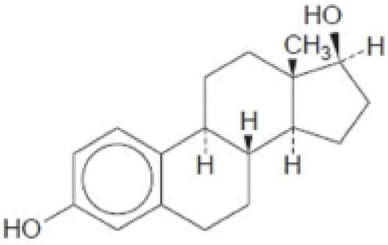
4)Chemists use skeletal or partial-skeletal formulae to represent larger structures. For example the structure



may also be represented as follows.



Oestradiol is one of the hormones that controls the reproductive cycle in female mammals.



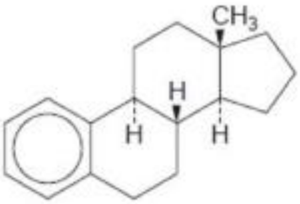
oestradiol

(a) (i) On the above structure of oestradiol, circle one chiral centre.

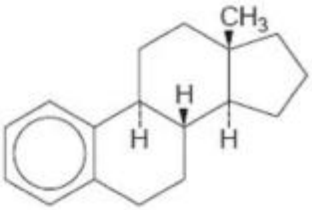
(ii) What is the total number of chiral centres in the oestradiol molecule?

5)(a) Complete the following part-structures (which have the -OH groups removed) to show the products obtained when oestradiol (above) is reacted with the stated reagents.

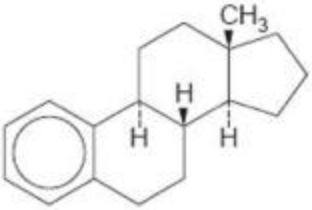
(i) sodium metal



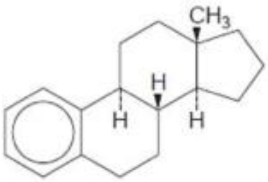
(ii) $Br_2(aq)$



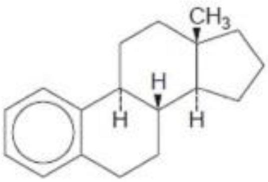
(iii) NaOH(aq)



(iv) CH_3COCl



(v) hot acidified $K_2Cr_2O_7$

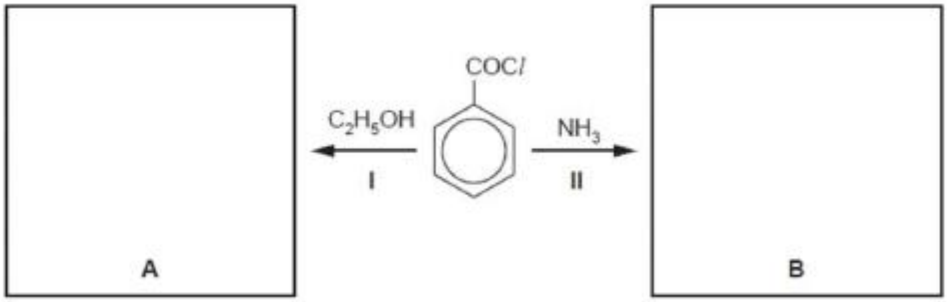


6)Acyl chlorides are useful intermediates in organic syntheses.

(a) (i) State a suitable reagent for converting carboxylic acids into acyl chlorides.

(ii) Construct an equation for the reaction between ethanoic acid, CH_3,CO_2H, and the reagent you have stated in (i).

(b) (i) In the boxes provided draw the structures of the compounds formed when benzoyl chloride undergoes the following reactions.



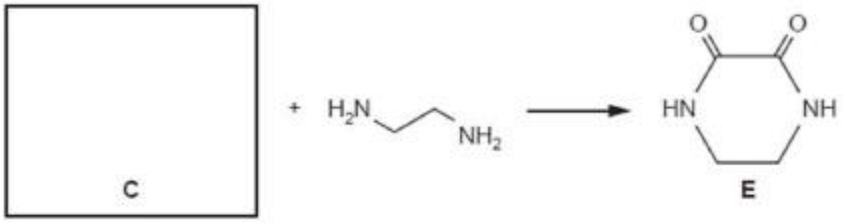
(ii) Name the functional group in

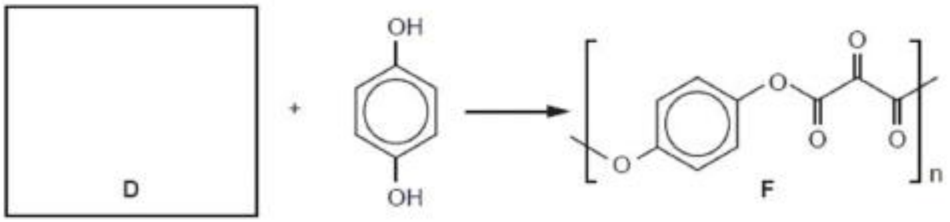
compound A

compound B

(iii) What type of reaction is reaction II?

(c) (i) Suggest suitable acyl chlorides to use in the following reaction. Draw their structures in the boxes provided.





Compound E dissolves in, but does not react with, cold water.

(ii) Suggest the major type of intermolecular interaction that occurs between E and water.

(iii) A solution of the diamine $H_2NCH_2CH_2NH_2$ in water has pH = 11 but a solution of E in water has pH = 7. Suggest why this is the case.

(iv) What type of polymer is compound F?

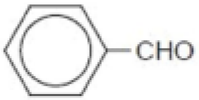
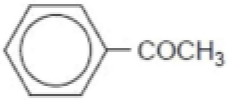
7) (a) The reaction producing tri-iodomethane (iodoform) can be used as a test for the presence of certain groups within a molecule.

(i) State the reagents and conditions used for this reaction.

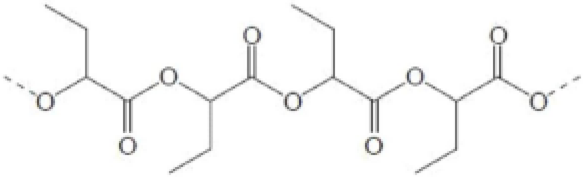
(ii) Write the structural formula of one functional group that would give a positive result with this iodoform reaction.

(iii) What do you observe in a positive test?

7) In the following table place a tick (✓) in the column against each compound that would give a positive result with this test, and a cross (X) against each compound that would give a negative result.

compound	result
CH_3OH	
CH_3CH_2OH	
CH_3CHO	
CH_3CO_2H	
	
	

8)The following diagram represents a section of another polymer.



D

(i) On the above formula draw brackets, [ ], around the atoms that make up the repeat unit of this polymer.

(ii) Name the functional group in polymer D.

(ii) Suggest and draw the structure of the monomer, E, that could form this polymer.

(iv) What type of polymerisation is involved in making polymer D from its monomer?

(v) What is the relationship between the repeat unit of polymer D and the repeat unit of PVA?